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Title: The Path to Nitrate Salt Disposition

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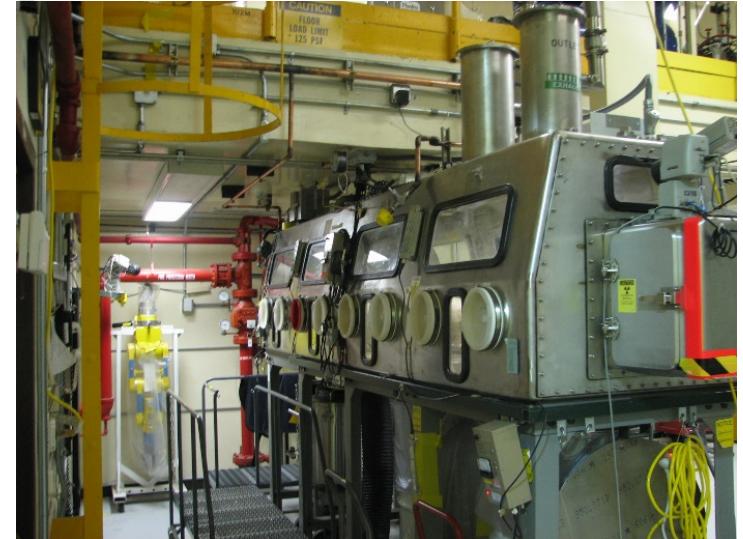
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The Path to Nitrate Salt Disposition

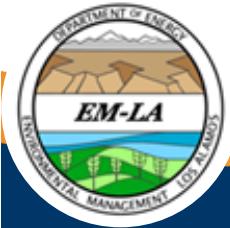
Dave Funk

February 22, 2016

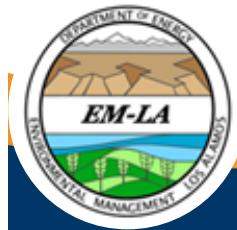
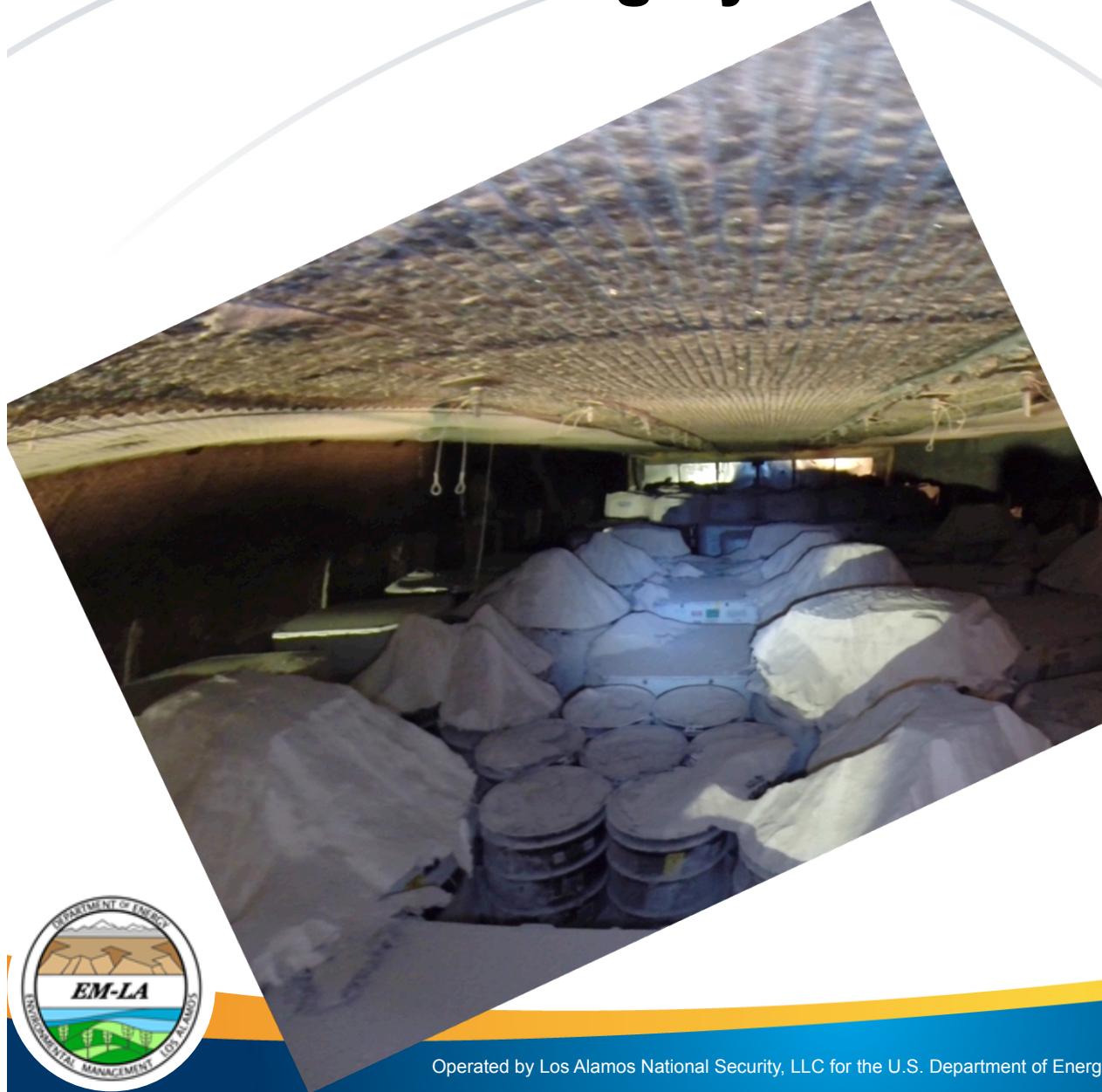


Outline

- LANL Nitrate Salt Incident as Thermal Runaway
 - Thermally sensitive surrogates
 - Full scale tests
- Temperature Control for Processing
- Treatment Options and Down Selection
- Assessment of Engineering Options
- Anticipated Control Set for Treatment
- Summary of the Overall Steps for RNS Treatment

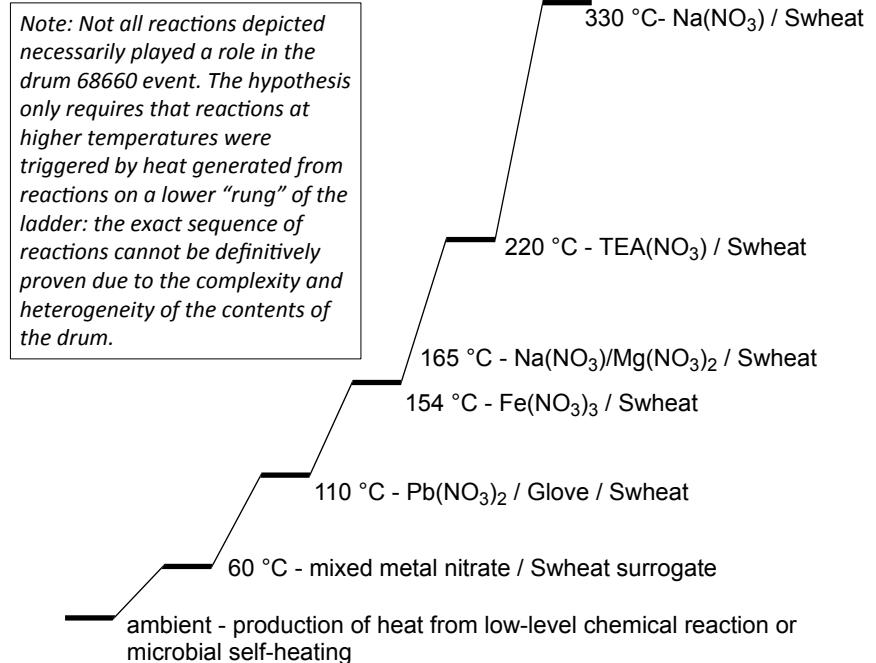


Incident was identified by rad release and imagery from the mine



Summary Description of the LANL Nitrate Salt Incident

- The incompatibility of the nitrate salt (oxidizer) and Swheat kitty litter (fuel) mixture, created the potential for thermal runaway that was ultimately realized when Drum 68660 pressurized and breached
- Production of heat, either from low-level chemical reactions or the growth of natural microbes, in concert with mixed metal nitrate salts, bismuth lined glovebox gloves and/or lead nitrates when combined with the Swheat organic kitty litter, generated a series of exothermic reactions that heated and pressurized the drum resulting in the venting of high-temperature gases and radioactive material into the room.

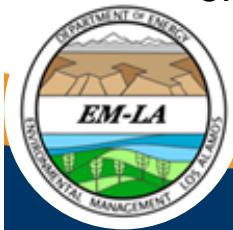
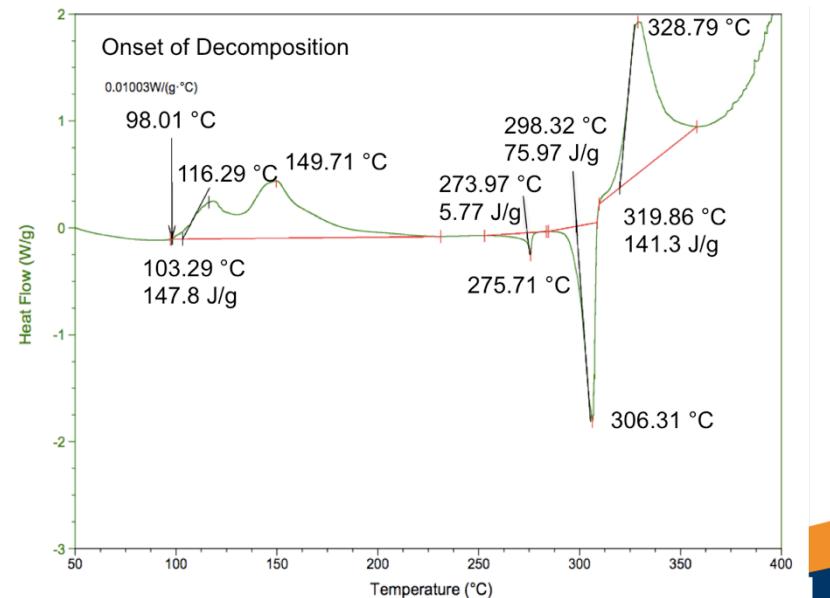


Our current thinking: the chemical incompatibility lead to thermal runaway through low temperature reactions



Technical studies identified increased nitrate salt/swheat thermal sensitivity with complex mixtures

- Na(NO₃)/Swheat – 330 °C
- HTEA(NO₃)/Swheat – 220 °C
- Na(NO₃)/Mg(NO₃)₂/Swheat – 165 °C
- Fe(NO₃)₃/Swheat – 154 °C
- Pb/TEAN/Swheat – 110 °C
 - 1M HNO₃ – no change in decomposition onset
 - 8M and 16M HNO₃ – new exotherm
- Bi-lined glove/Nitrate/Swheat – 110 °C
- Bi-lined glove/TEAN/Sweat
 - 1M HNO₃ – no change in decomposition onset
 - 8M and 16M HNO₃ – new exotherm



Thermochemical modeling of processes yielded most sensitive surrogate salt mixtures

- Stream Analyzer (OLI) software used to model the evaporator processes
- The derived mixtures of metal nitrate salts with Swheat show:
 - Low exotherm temperatures **30-55 °C**
 - Evidence of incompatibilities leading to decomposition and NO, NO₂ evolution, followed by Swheat nitration (as high as 6-7%)
 - Material that exhibits some electrostatic discharge sensitivity
 - Mg, Fe, and Pb appear to be the main contributors to these processes
- Prepare actinide sample through spiking, use of UNS samples

Table 1. Important metal ion concentrations (median values) in evaporator bottoms from Veazey, et al.² (in g/l)

	Ion Exchange	Oxalate Filtrate
Ca	61	10.5
Mg	58.7	13.3
K	17.6	4.8
Fe	17.0	7.9
Na	7.4	23.9
Al	4.6	2.3
Cr	3.0	1.94
Ni	1.8	1.205
Pb	0.19	0.056



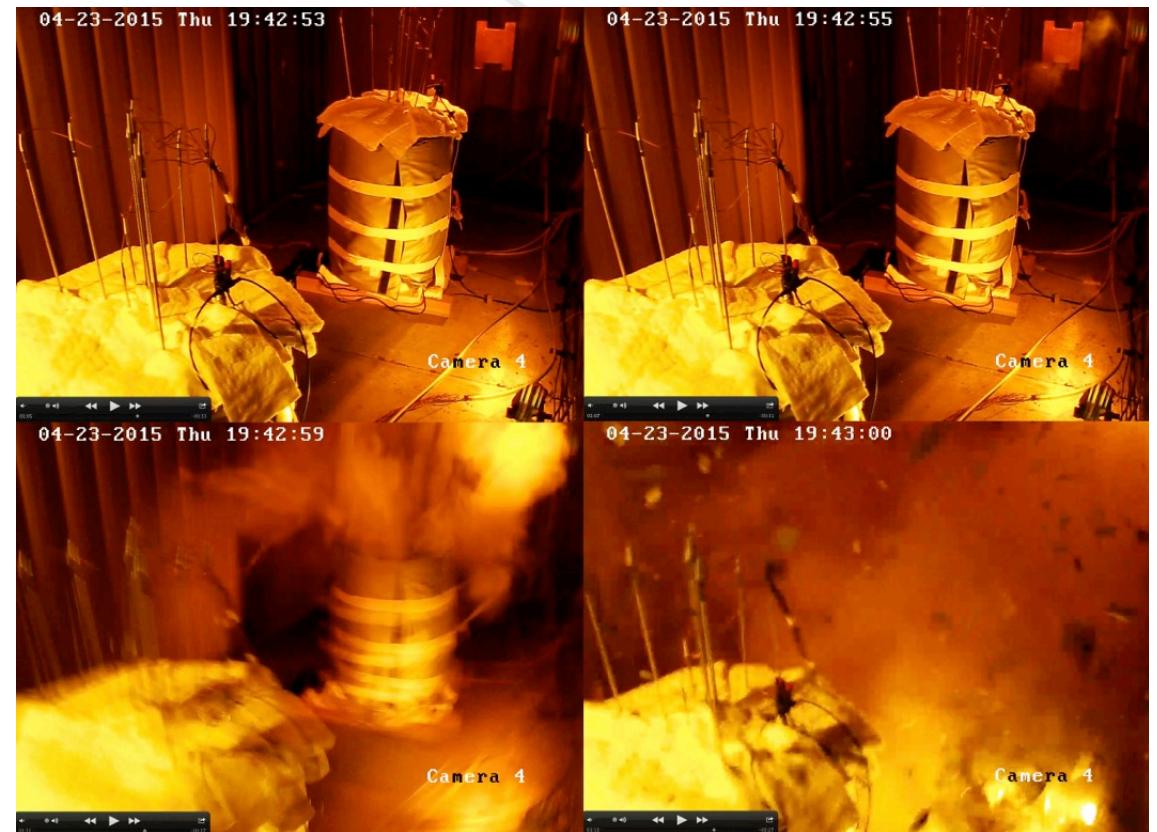
Veazey, G. W.; Castaneda, A. *Characterization of TA-55 Evaporator Bottoms Waste Stream*; NMT-2:FY 96-13; Los Alamos National Laboratory: Los Alamos, NM, 1996



The full scale drum tests were of significant technical value



- Requested by the AIB to support their investigation
- A goal was to demonstrate that we have an understanding of the mechanisms by which the 68660 breach may have occurred
- Provided valuable insight to guide the storage and processing of existing nitrate salt bearing drums processed with Swheat

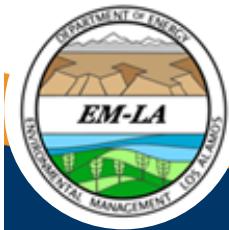


The Thermolytic Response of a Surrogate RNS Waste Mixture at the Drum Scale

Gary Parker, Matt Holmes, Eric Heatwole and Peter Dickson
M-6, HE Thermal and Mechanical Response Team

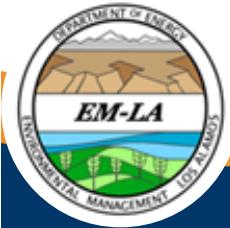
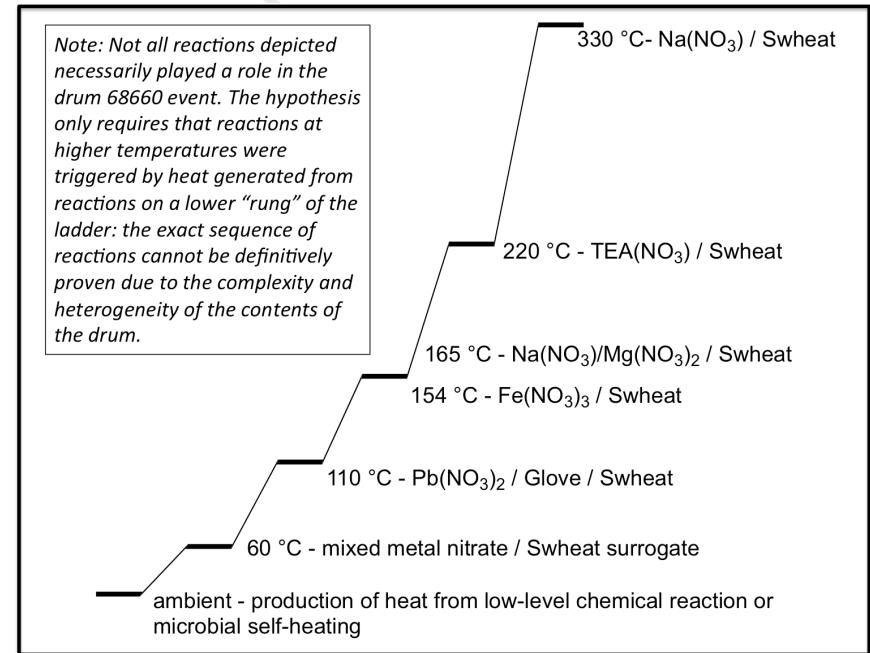
Phil Leonard
M-7, HE Science and Technology

Chris Leibman
C-CDE, Chemical Diagnostics and Engineering



Technical Objectives

- Perform long duration, drum-scale tests with a plausible surrogate and physical arrangement.
- Test hypothesized “ladder” of plausible exothermic reactions
- Diagnose the thermal response of the drums; evaluate the effect of compositional inhomogeneity
- Evaluate the effect of pressure
- Perform headspace gas compositional analysis
- Record video and audio



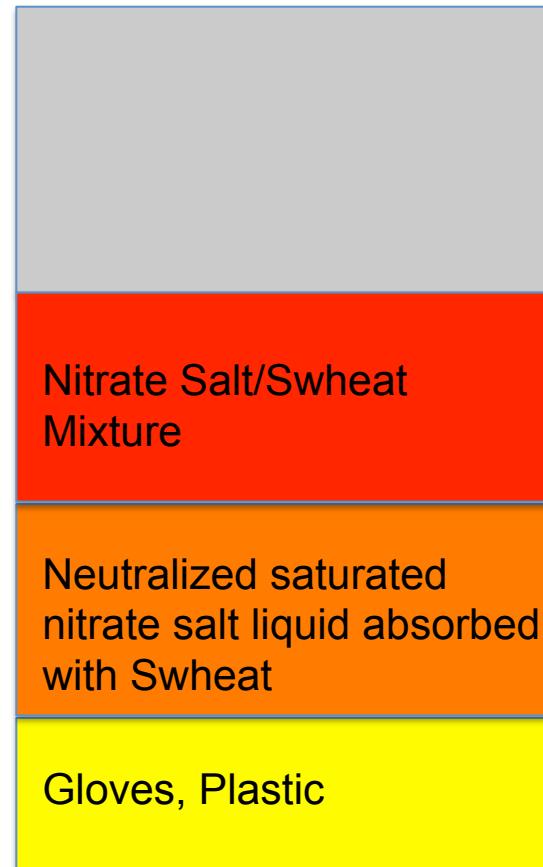
Demonstrate Thermal Runaway from Plausible Initial Conditions



- Be reasonably faithful to the drum contents
 - Variety of nitrate salts
 - Swheat Scoop pet litter
 - No radioactive components
 - Include Pb
 - Liquid neutralized with Kolorsafe Spilfyter
 - Generates triethanolammonium nitrate (TEAN)
- Include known components and prep as expected in WCRRF (layers)
 - Bi-W-La gloves, Spilfyter container



Sketch of Contents, Based on RTR



Experiment Variables



1. Boundary Temperatures: 25°C and 60°C

- Average temperature at WIPP is ~25°C.
- Use elevated boundary temperature of 60°C as an accelerated rate test.
 - Long term chemical activity or biological activity could have elevated the temperature.

2. Pressure: Vented and Sealed

- Standard drum configuration contains a “nucfil” filter with a carbon frit, designed to allow gas escape and prevent pressurization.
- #68660 may have become sealed:
 - Permeability of carbon filter is insufficient for high flow-rates.
 - Internal PVC plastic bag liner may have sealed against the outlet.
 - Bags of Magnesium Oxide piled on top covered/sealed filter outlet.
 - Solids/liquids/condensation produced from chemical activity may have clogged the carbon filter.



3. Chemical Composition: Weisbrod-8 (fixed)

- Selected—based on reactivity—to be most likely to result in a violent outcome, yet still a plausible composition for 68660.



Test Matrix

	Drum A	Drum B	Drum C	Drum D
Temperature	25°C	25°C	60°C	60°C
Pressure	Vented	Sealed	Vented	Sealed

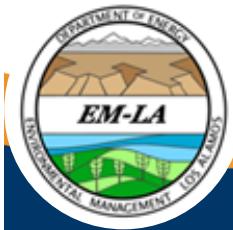


Nominal for WIPP



Accelerated case

- Conditions are bounding with respect to temperature and pressure.
- Surrogate formulation is not bounding, but is plausibly reactive



Experiment Layout

Two transportainers, two drums in each transportainer



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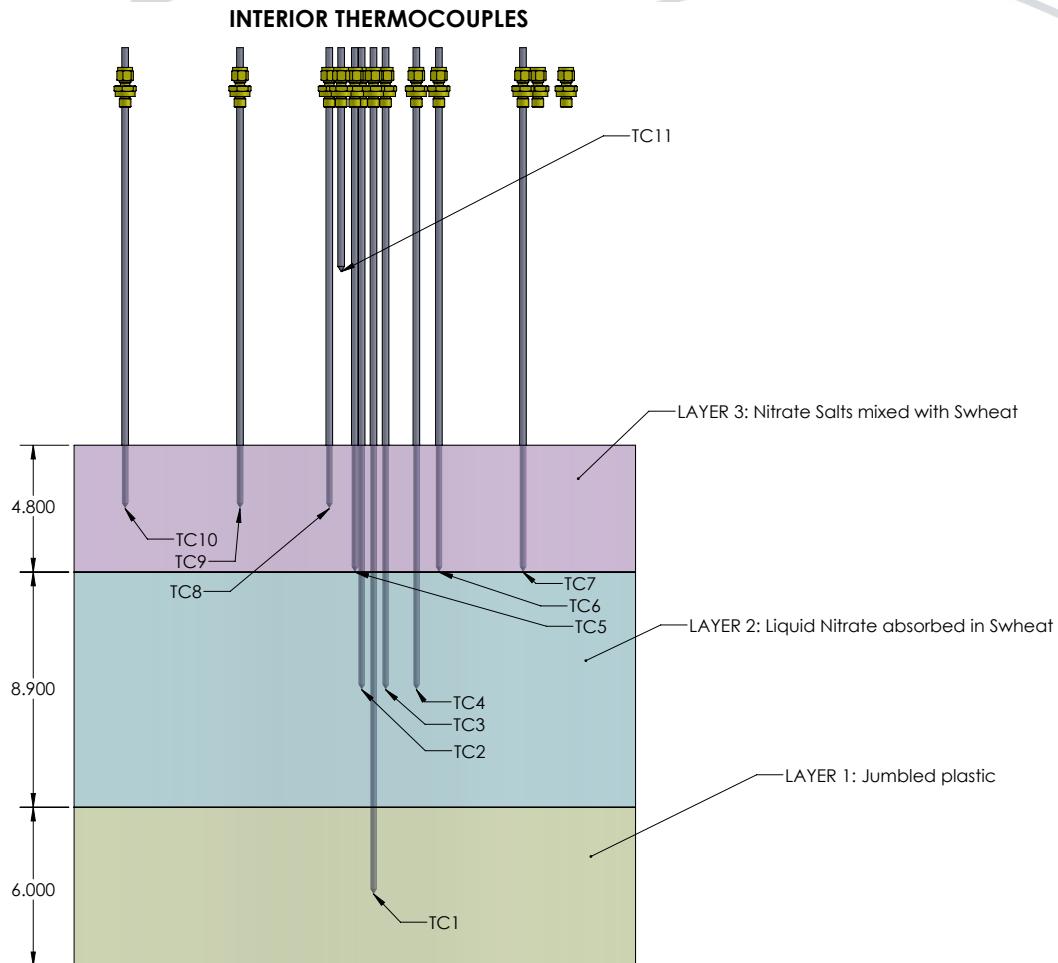
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Diagnostics

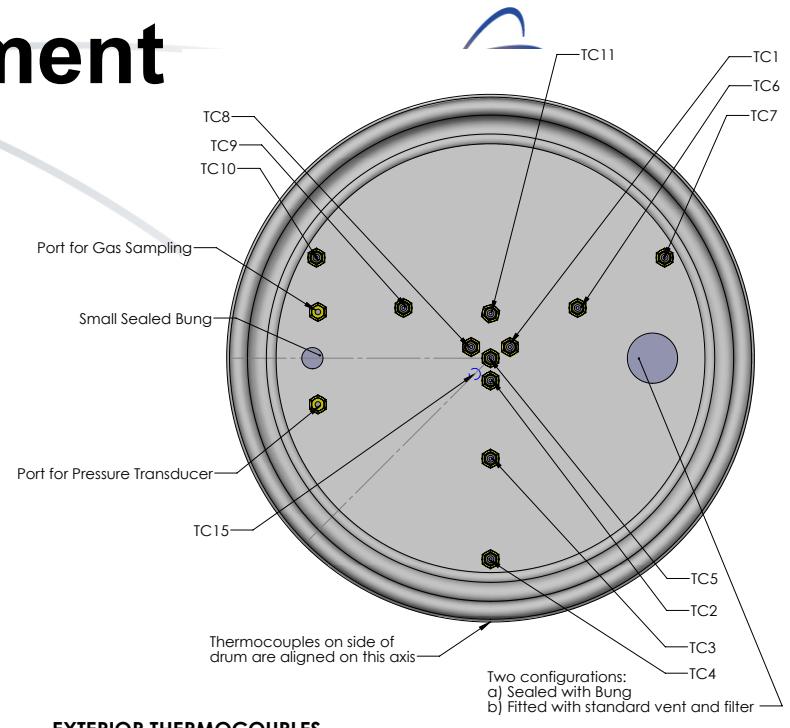
- Temperature
 - 21 thermocouples on each drum, 2 air temperature TCs
 - Spatially and temporally resolve the thermal response
- Pressure
 - Static transducer to measure the drum pressure as product gases evolve
 - Dynamic transducer to quantify the dynamic response
 - Ambient static pressure gauge monitoring barometric pressure of container
- Video
 - Eight surveillance cameras with constant real-time footage recording.
 - Overview surveillance of transportainers and surrounding environment
- Headspace gas sampling
 - Conducted remotely through a ~30ft tubing run



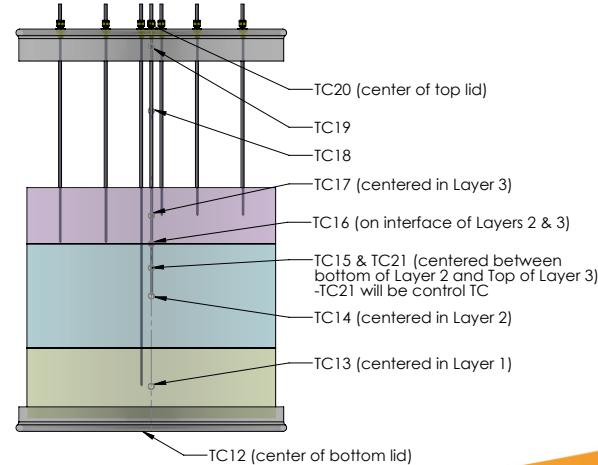
Thermocouple Arrangement



Three layer composition, filling ~60% of barrel
(derived from RTR of 68660)



EXTERIOR THERMOCOUPLES



Drum Preparation Photographs



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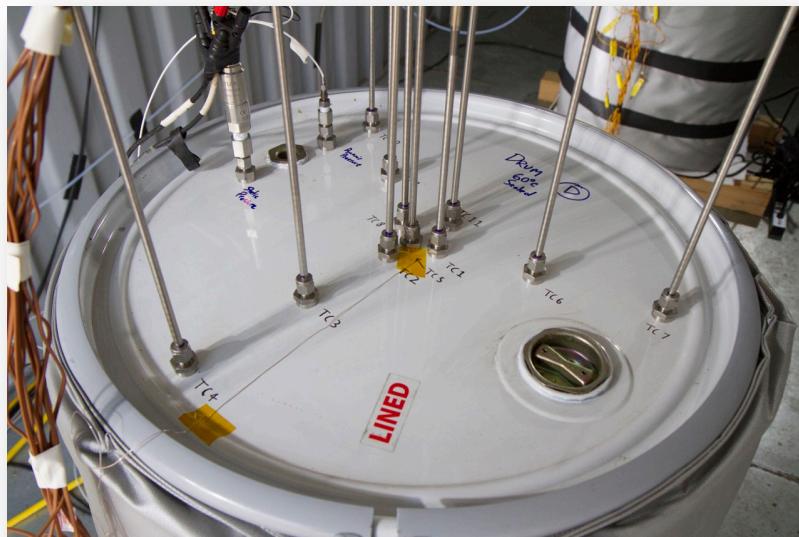


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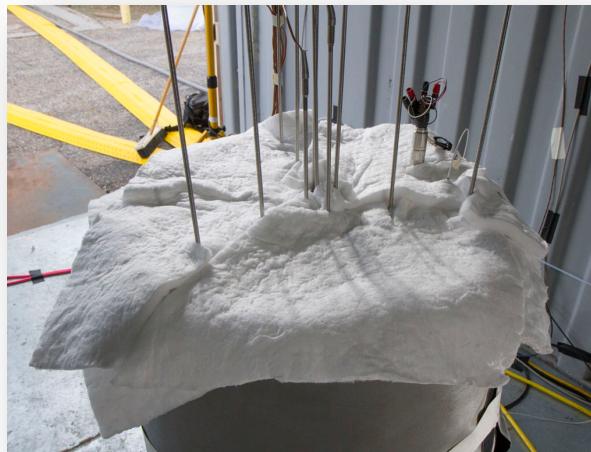
Drum Preparation Photographs (cont.)



Lid was fastened with a clamping ring that was bolted closed with a specified torque. Lid seal functioned within design spec, withholding pressure of 30 +/- 3 psi.



Drum Preparation Photographs (cont.)



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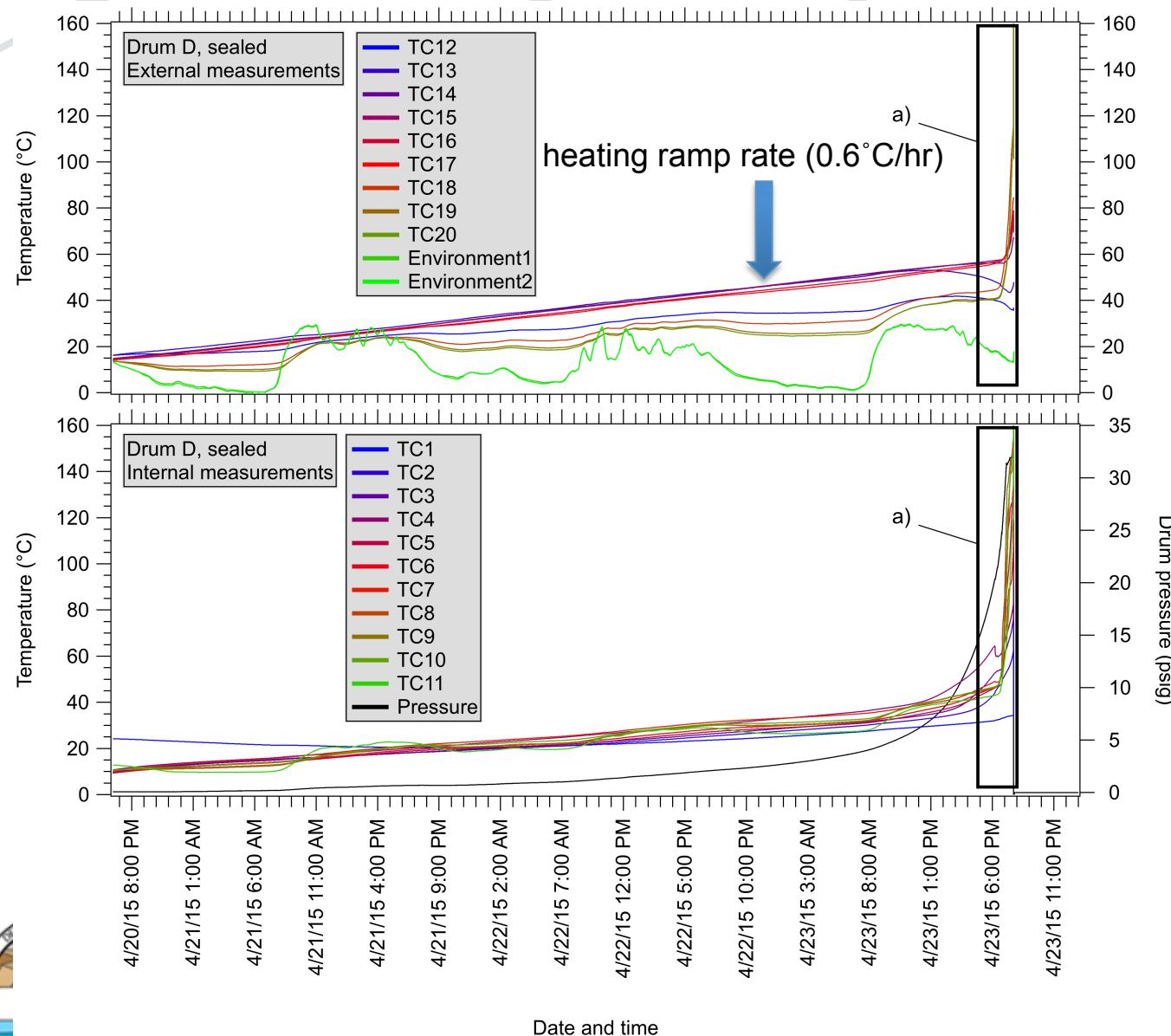
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Results

Drum D



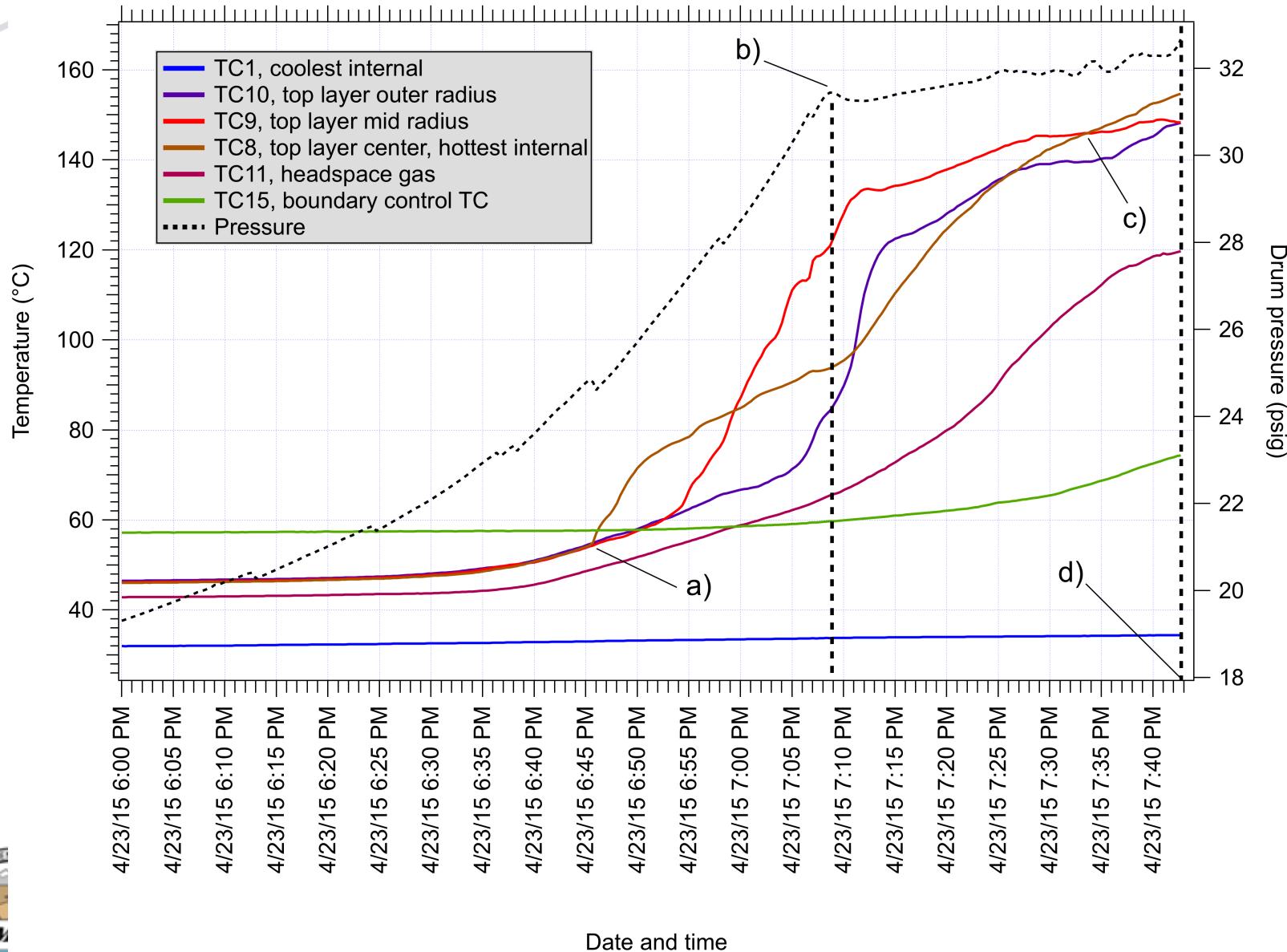
Drum D (60°C, sealed): Full dataset



This purpose of this test was to explore a drum with a blocked vent and at elevated temperature to jumpstart and accelerate the chemistry.



Drum D (60C, sealed)—Detail



Drum D: Post-Mortem Images



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Drum D: Summary

- Pressure burst occurred in ~3 days (73.3 hrs) in a sealed & heated configuration with the SFWB-8 composition
 - Physical explosion
- Event precursors:
 - Noticeable bulging of lid and base (slowly over the ~3 hrs prior to burst)
 - Considerable fumes (~30 mins prior to burst)
 - Audible indication (~30 mins prior to burst)
- No flame was observed during the burst
- Lid seal failed in a controlled manner at 32 psi, maintaining pressure



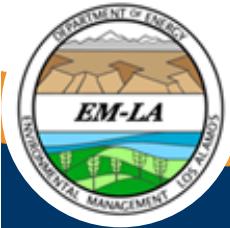
Drum D: Discussion

- When lid seal vented, thermal runaway slowed
 - Evidence for importance of gas-phase reactants on exothermic chemistry
 - Orange vapor is evidence for NO_2 production
- Hottest location in top layer, high headspace gas temp.
 - Also evidence for the importance of gas-phase reactants
- No scorching. Did not get as hot as Drum 68660
 - Did not have MgO sacks weighing down the lid
 - Reaction was quenched when lid blew off, what if it had been held in place?
 - Surrogate might have had more H_2O than drum 68660
 - Heat capacity and latent heat of vaporization

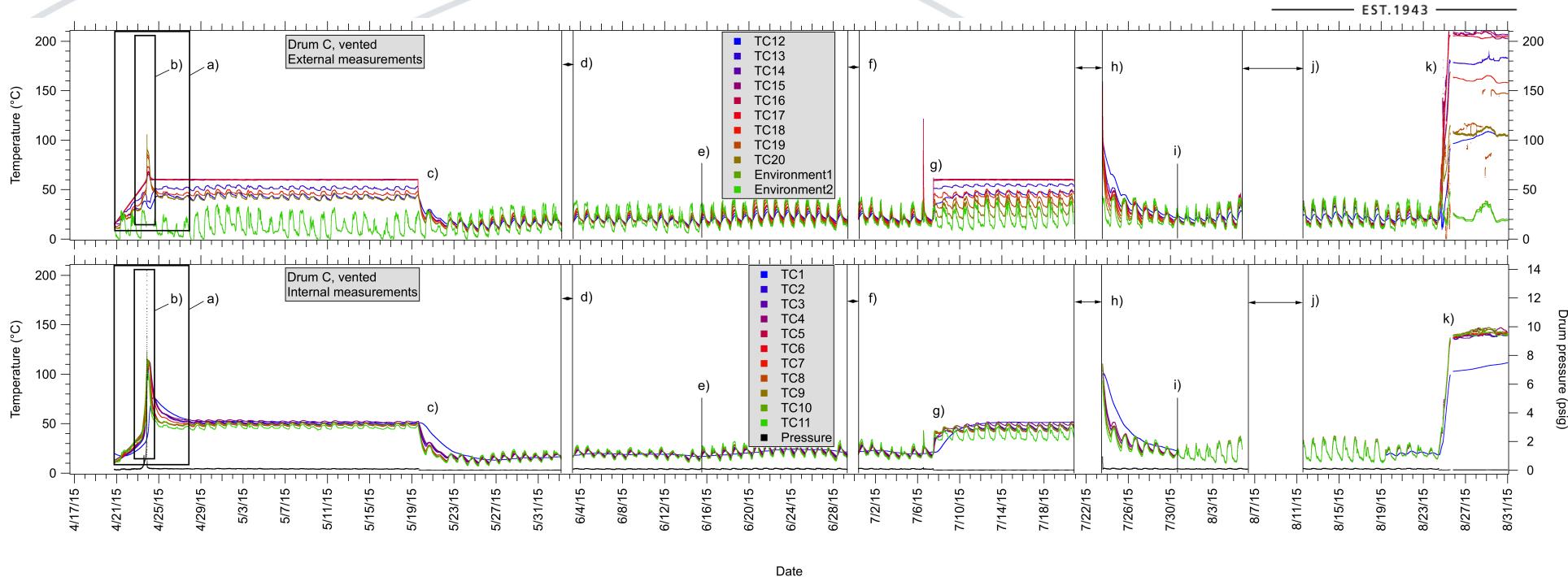


Results

Drum C



Drum C (60°C, vented): Full dataset



This purpose of this test was to explore a drum with a normal vent, but at elevated temperature to jumpstart and accelerate the chemistry



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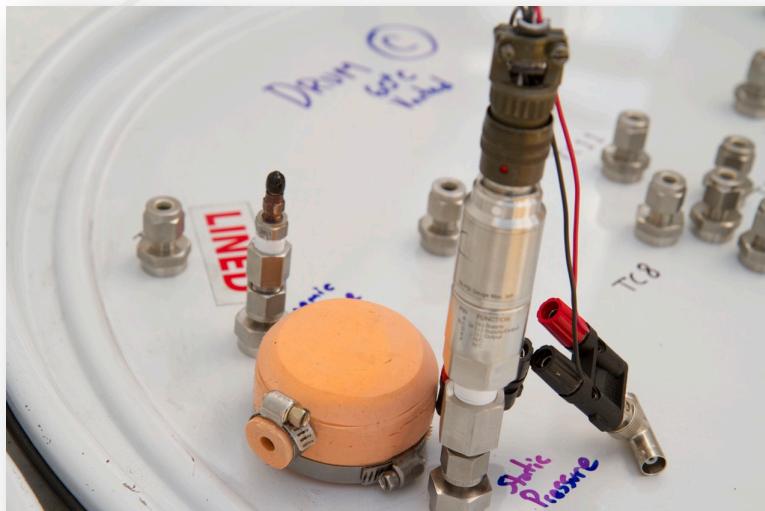


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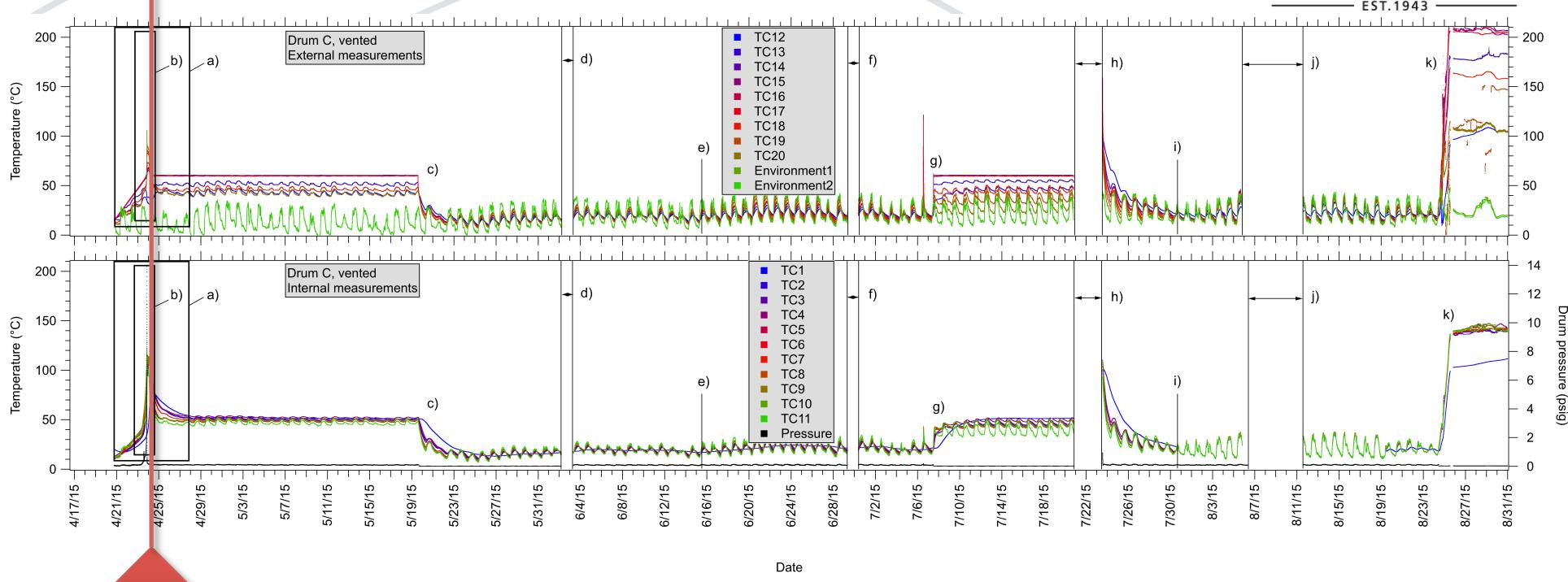
Drum C (60°C, vented): Full dataset



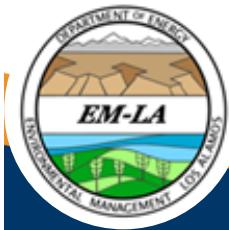
Headspace gas sampling cap was fit over the Nucfil filter.



Drum C (60°C, vented): Full dataset



Runaway-quench
event

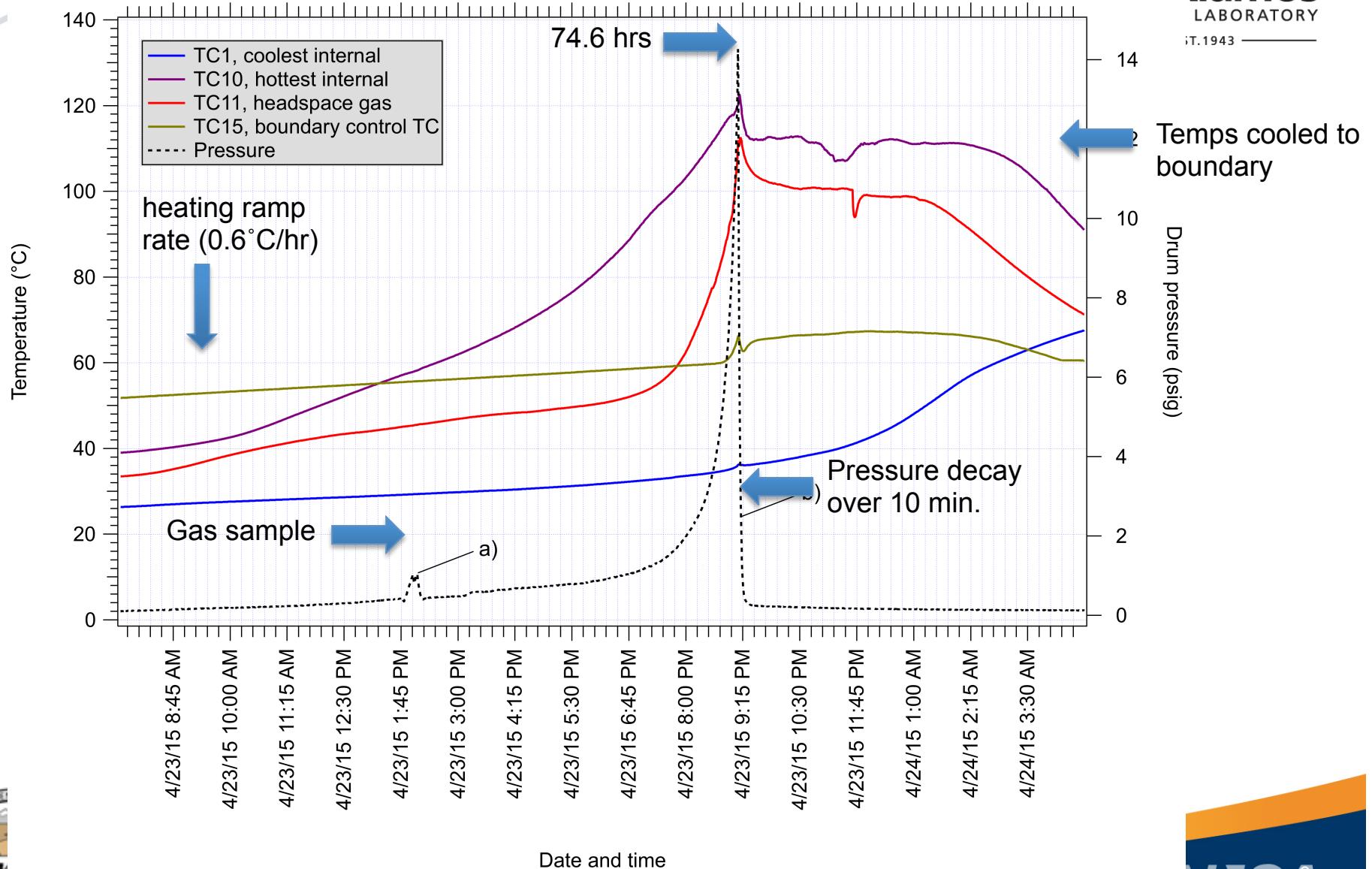


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Drum C (60°C, vented) runaway-quench event: detail



Drum C (60°C, vented): headspace gas analysis



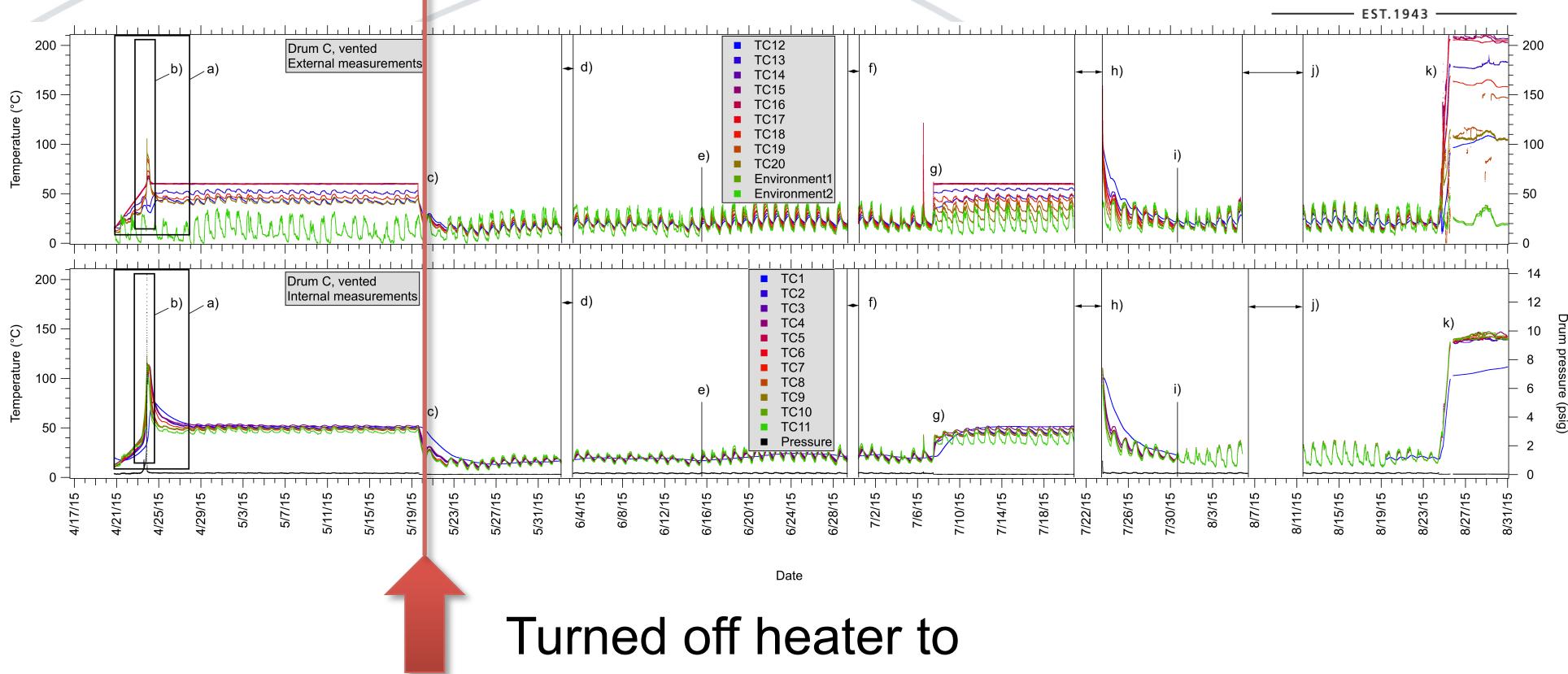
- Flow rate: >2 L/min
- The nitrogen observed is attributed to nitrogen from ambient air. Other gases observed were likely displacing the nitrogen as they were generated within the drum.
- Significant quantities of NO, N₂O and CO₂ were measured.
- Oxygen was not detected in the sample above the reporting limit of 30 mtorr.
- NO₂ cannot be measured directly with the GC/TCD, though pressure balance might indicate very little concentration.

	Gas Partial Pressure (Torr)	% of Drum Headspace	Product Gas Fraction Excluding N ₂ (%)
Helium (He)	N.D.		
Hydrogen (H ₂)	N.D.		
Oxygen (O ₂)	N.D.		
Nitrogen (N ₂)	72	50.7	
Nitric oxide (NO)	24.7	17.3	35.2
Carbon monoxide (CO)	3.1	2.1	24.4
Methane (CH ₄)	N.D.		
Carbon dioxide (CO ₂)	30.2	21.3	43.1
Nitrous oxide (N ₂ O)	12.2	8.6	17.4
Sum of partial pressures	142.2		
Paroscientific gauge pressure	143.8		
% difference	1.1		

*N.D. < 0.03 Torr



Drum C (60°C, vented): Full dataset

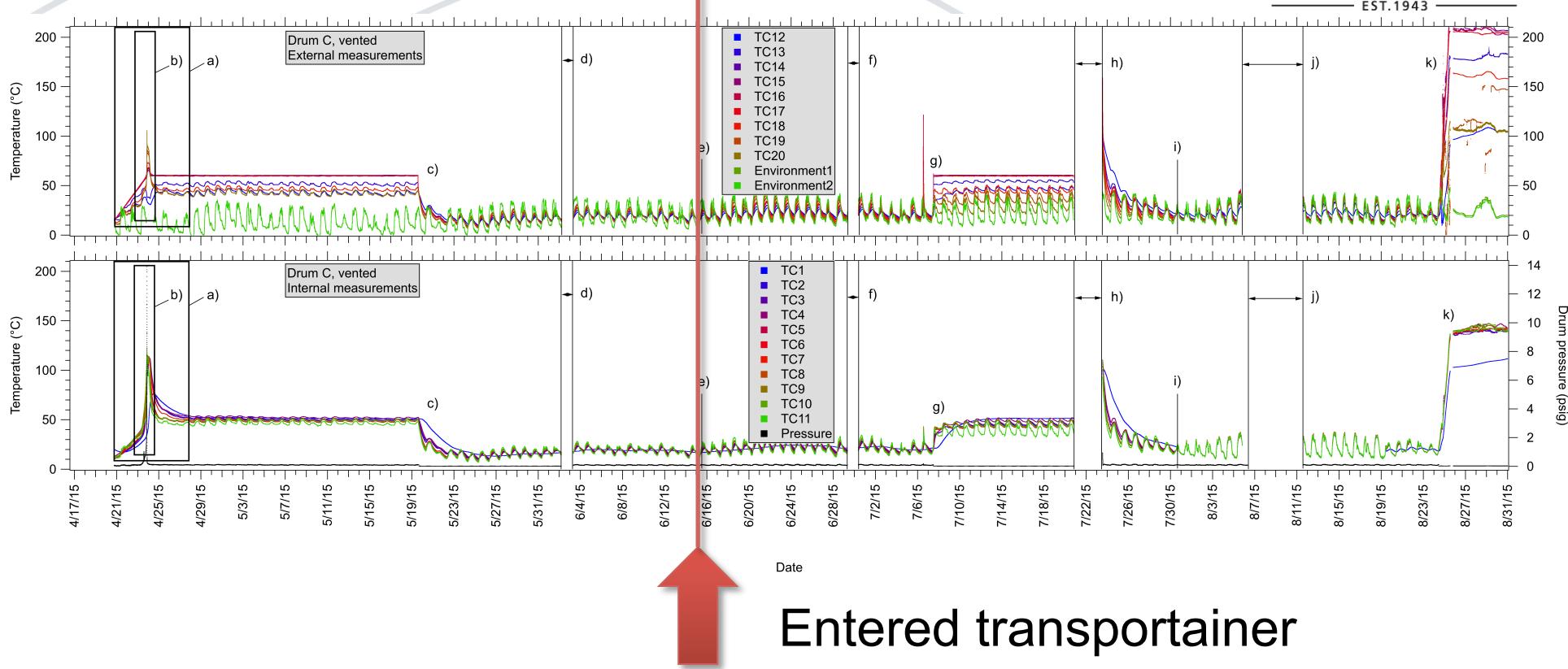


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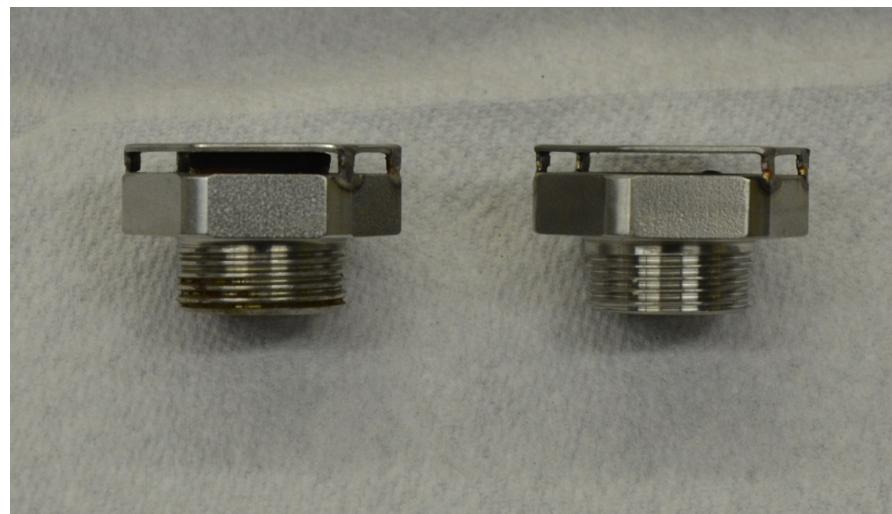


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Drum C (60°C, vented): Full dataset



Drum C: Pressure release

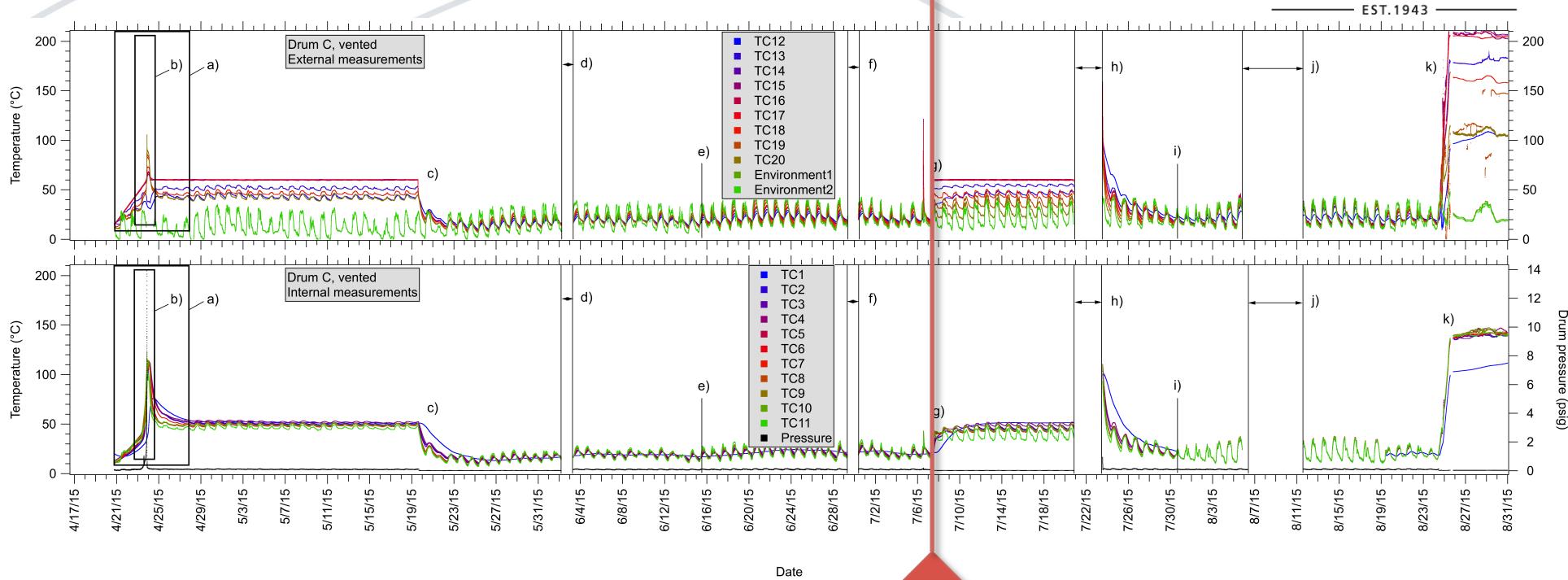


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Drum C (60°C, vented): Full dataset



Reheated to 60°C after replacing Nucfil filter, but not the gas sampling cap. No signs of reactivity.

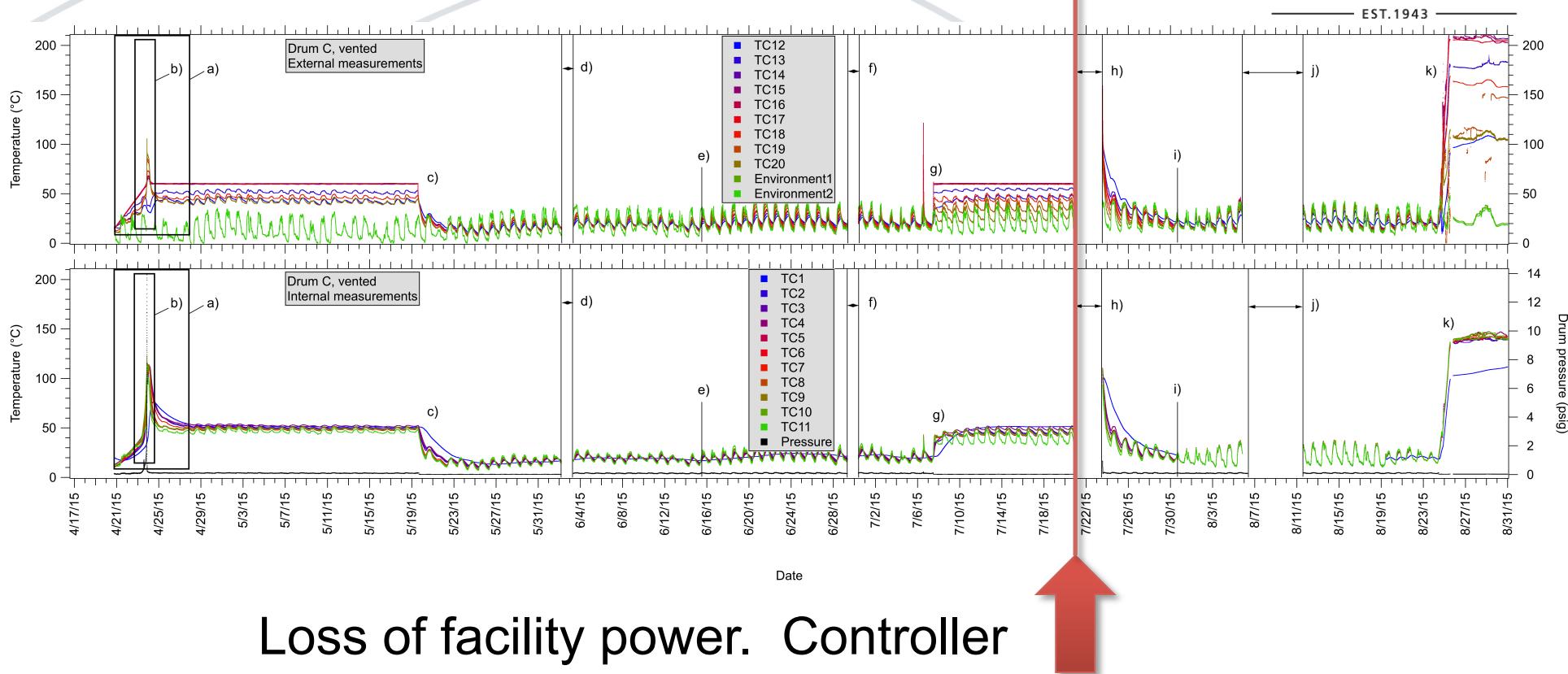


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Drum C (60°C, vented): Full dataset

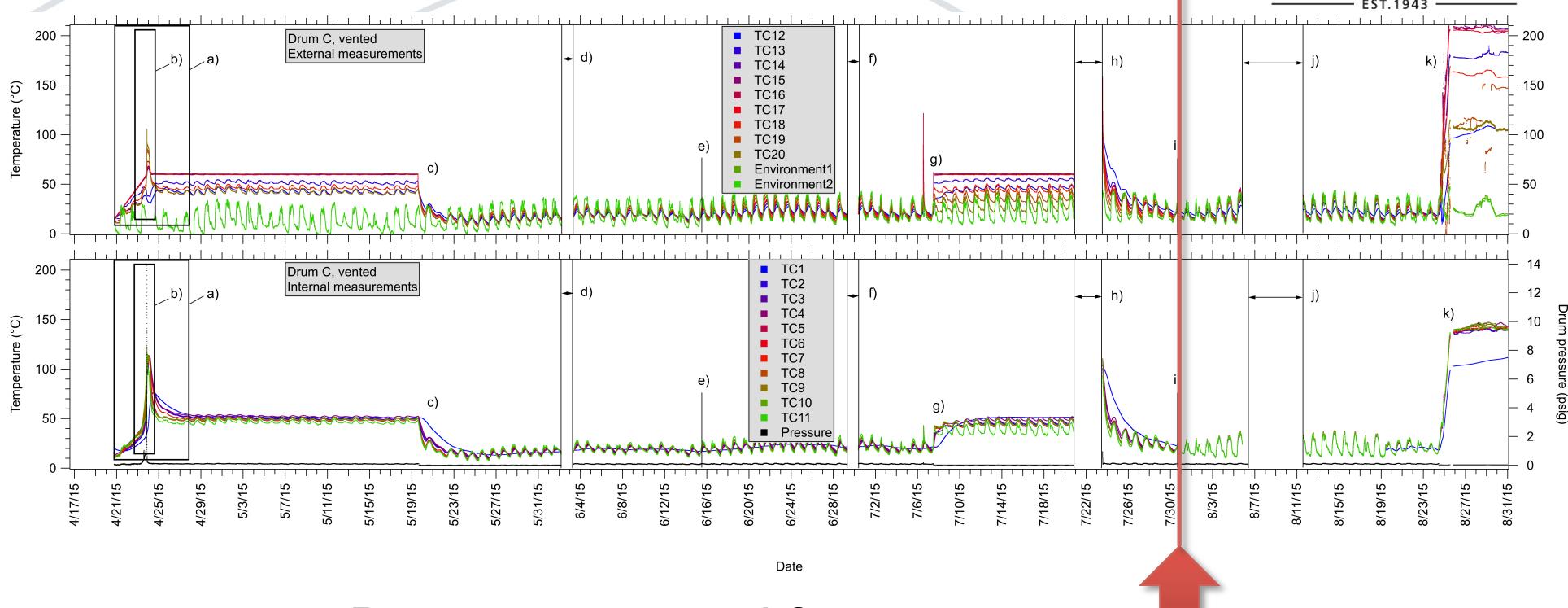


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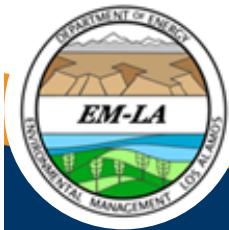


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Drum C (60°C, vented): Full dataset



Drum was opened for post-mortem examination



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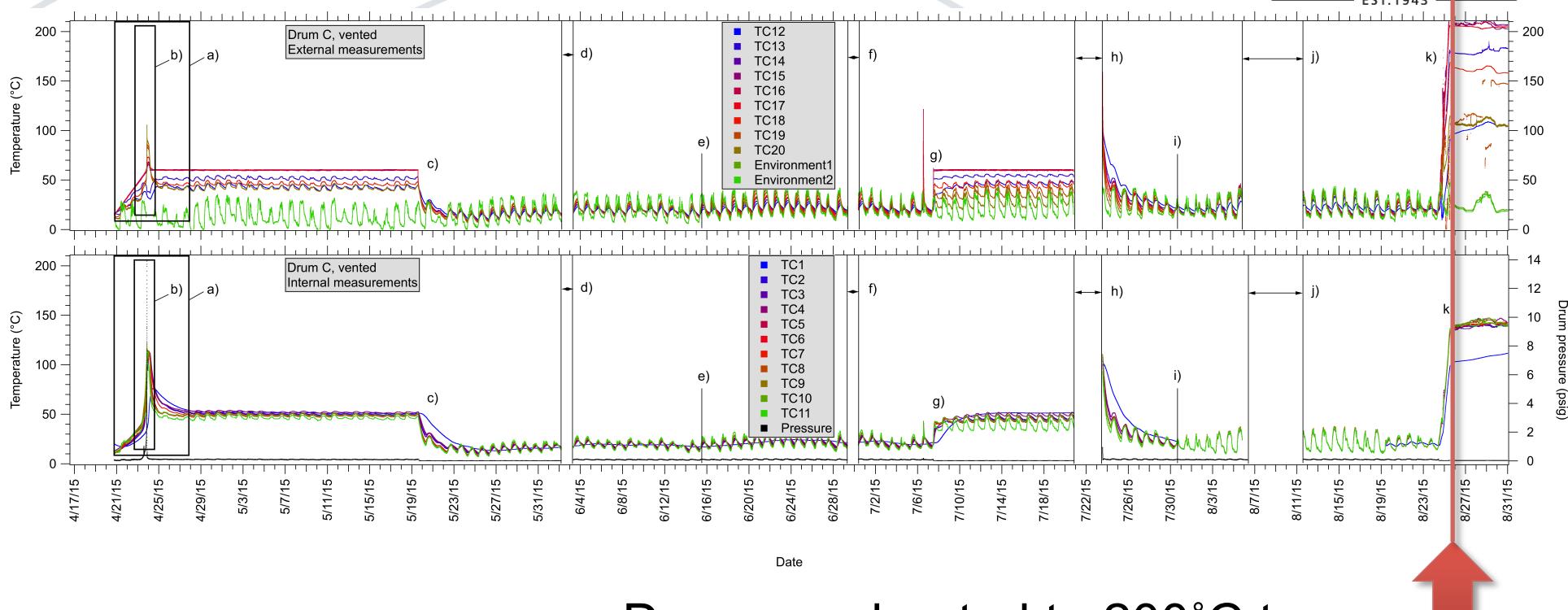
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Drum C: Post-mortem

- Lid was corroded
 - Seal had melted
- Bag yellowed
- Condensation present
- Contents were homogeneous, damp and sooty
 - Lighter colored powder is exfoliated cardboard from liner.



Drum C (60°C, vented): Full dataset

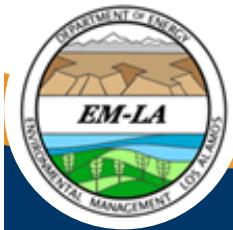


Drum was heated to 200°C to render the contents safe. No signs of reactivity during this phase of heating.



Drum C: Summary

- Pressure appears to be of paramount importance to the thermal runaway
 - Importance of gas-phase reactants attacking the solids
 - When pressure was relieved, runaway was quenched at 115°C
 - Flow restriction of the vent may be necessary for runaway to occur
- Pressure rise in vented drum due to some combination of:
 - Backpressure from gas sampling fixture
 - Restricted flow through carbon filter
- Hottest location in top layer, high headspace gas temp.
 - Also evidence for the importance of gas-phase reactants

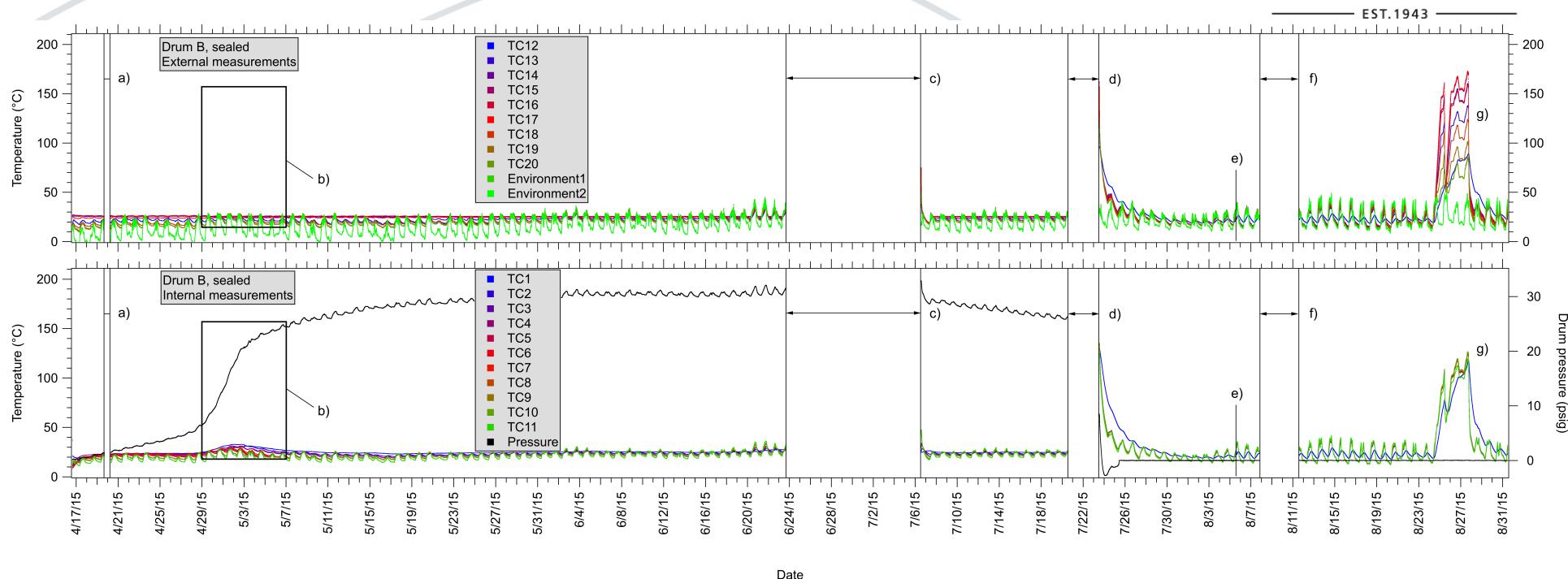


Results

Drum B



Drum B (25°C, sealed): Full dataset



This drum represents a drum stored under normal conditions in the WIPP, but explores the possibility of the vent having become blocked.

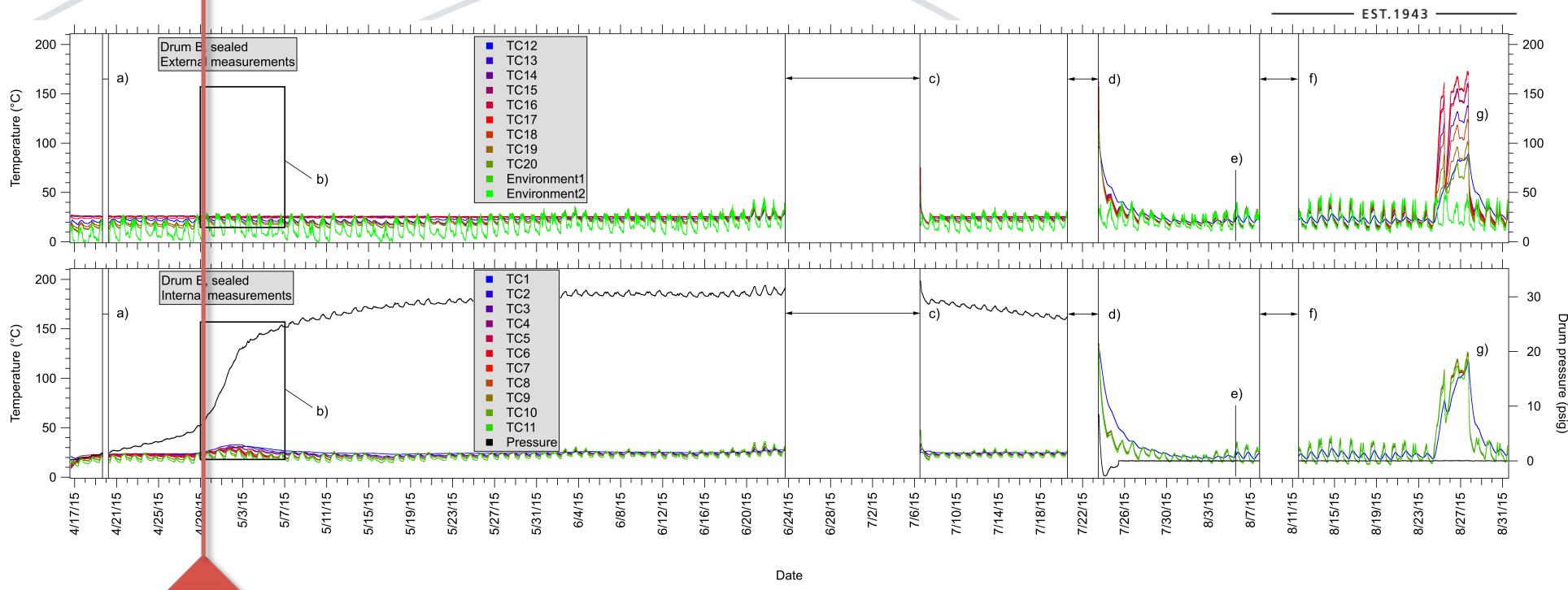


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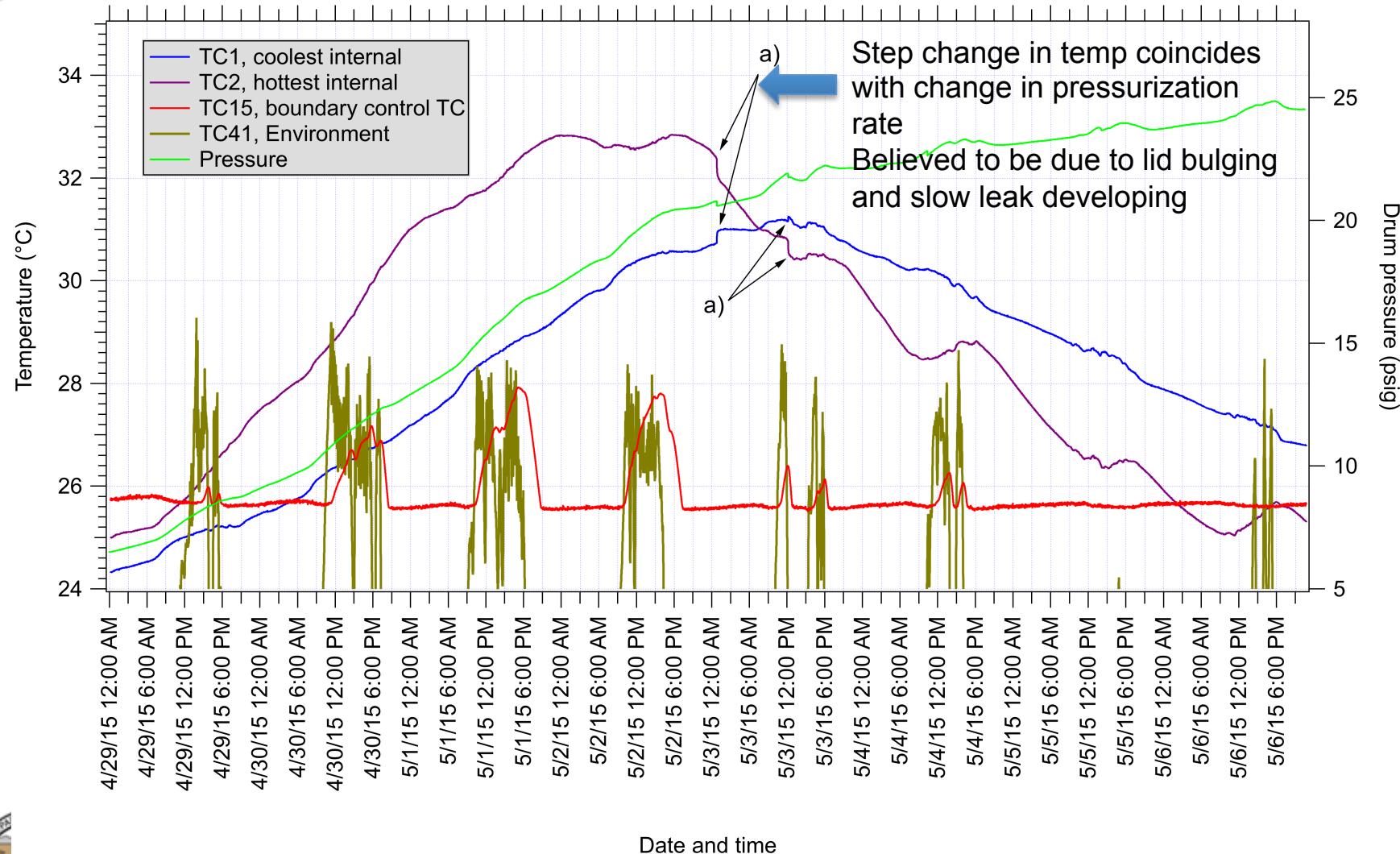
Drum B (25°C, sealed): Full dataset



Around day 12, saw the onset of self-heating and increased rate of pressurization, followed by quench. Interestingly, 12 days is the approximate duration that Drum 68660 was emplaced in the WIPP.



Drum B (25°C, sealed): Self-heating detail

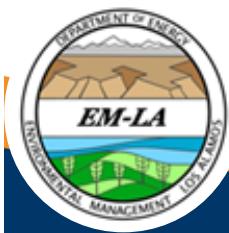
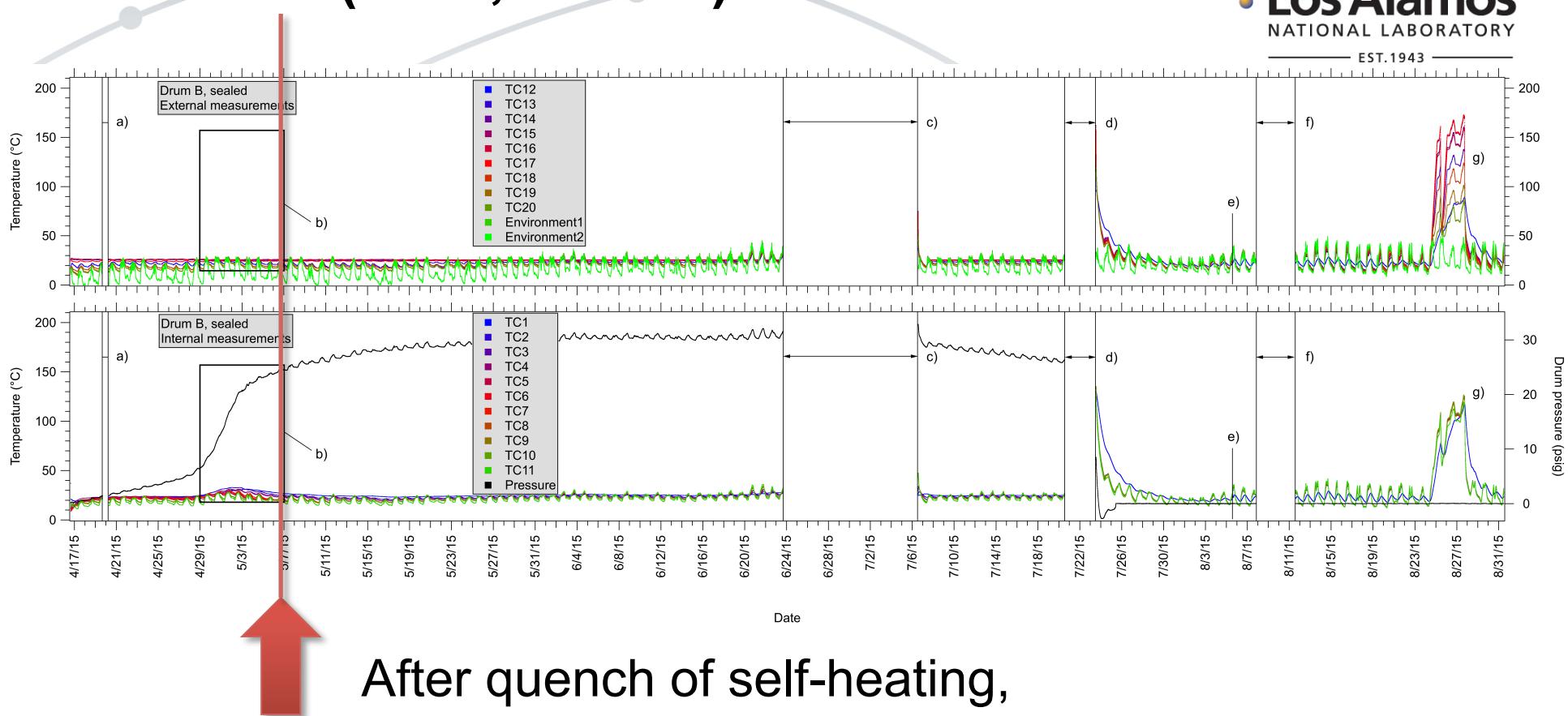


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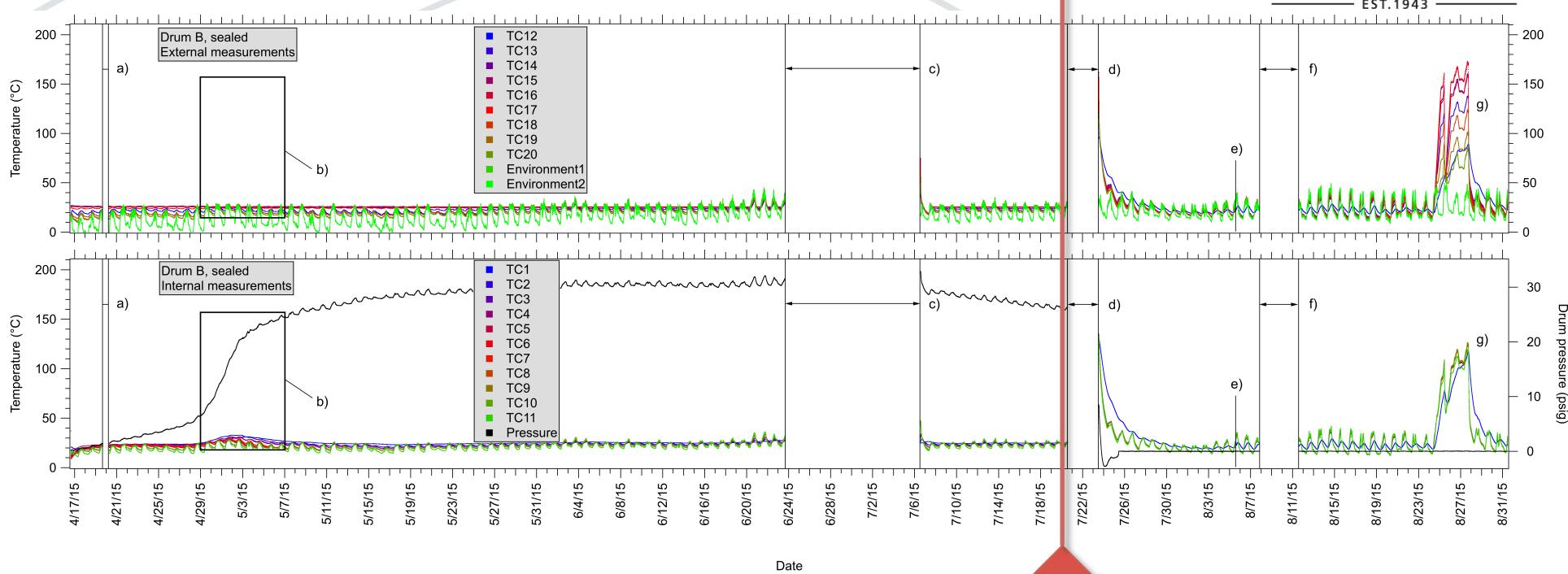


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Drum B (25°C, sealed): Full dataset



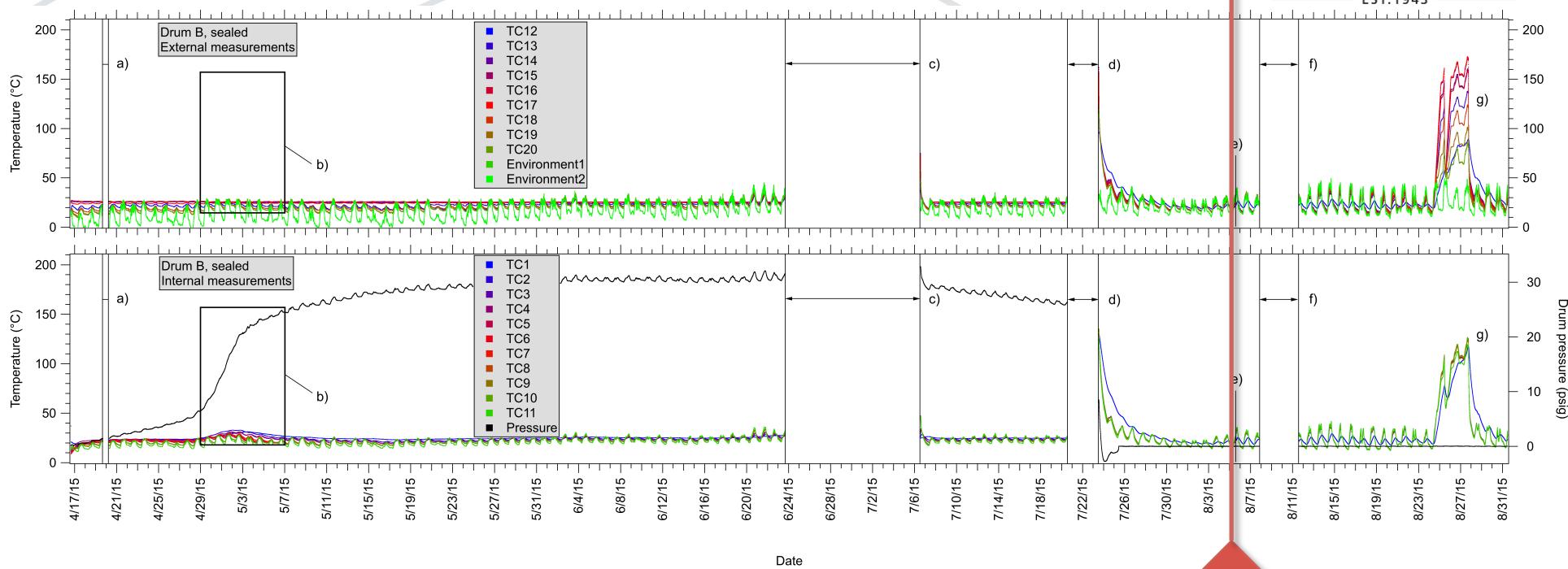
Drum B (25°C, sealed): Full dataset



Condition was stable for ~75 days, then the facility power was lost and the controller reset to 160°C.



Drum B (25°C, sealed): Full dataset



Drum was opened for post-mortem examination.



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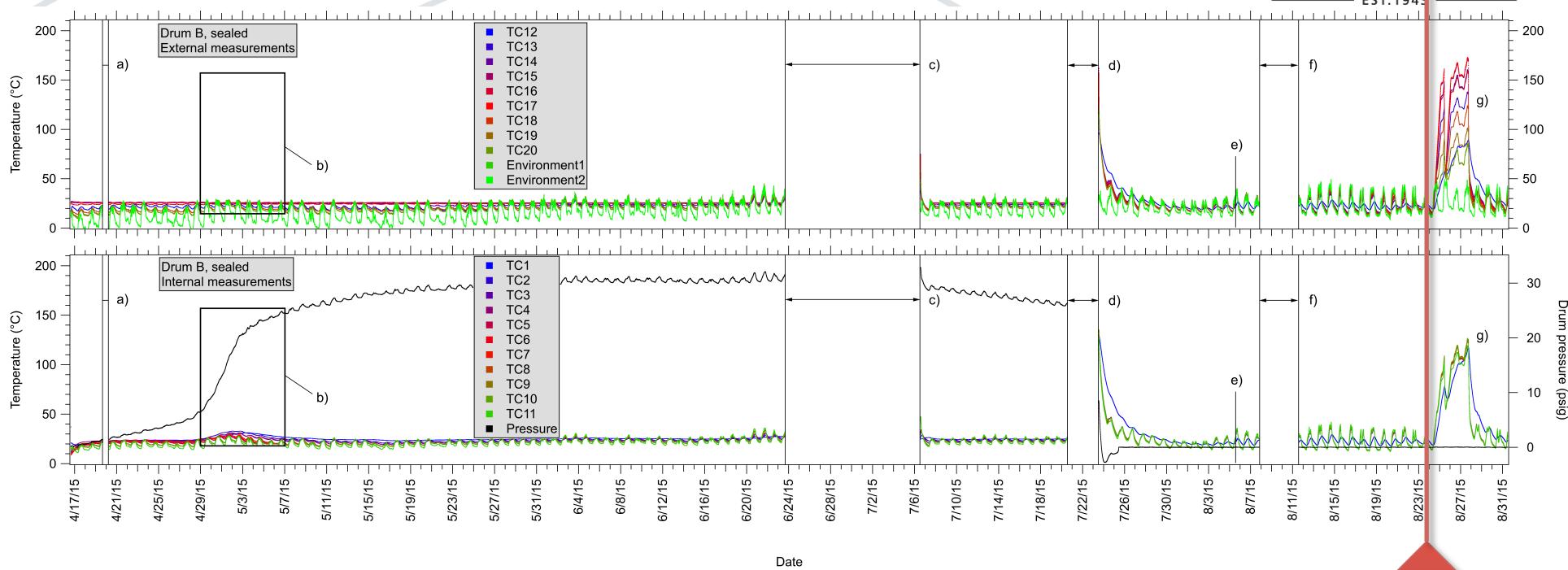
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Drum B (25°C, sealed): Post-mortem

- Lid was bulged
 - Lid seal failed
- Bag reddened and thermally damaged
- Contents were homogenous, dry and sooty
 - Material had slumped



Drum B (25°C, sealed): Full dataset



Drum was heated to 170°C to render the contents safe. No signs of reactivity during this phase of heating.



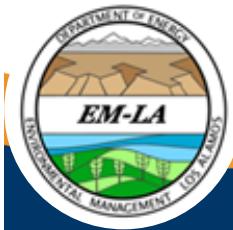
Drum B: Summary

- Reactivity and self-heating occurs at 25°C.
 - Self heating did not activate the next higher-temperature reaction(s) and quenched.
 - Low-rate, low-temperature reactivity depleted reactants.
- Quench of self heating coincident with venting of gas and pressure stabilization
 - Evidence for the importance of gaseous reactants.
- Upon heating to 160°C, there was evidence of combustion
 - Despite depletion of low-temperature reactants, higher temperature reactivity, or pockets of unreacted material, persisted.

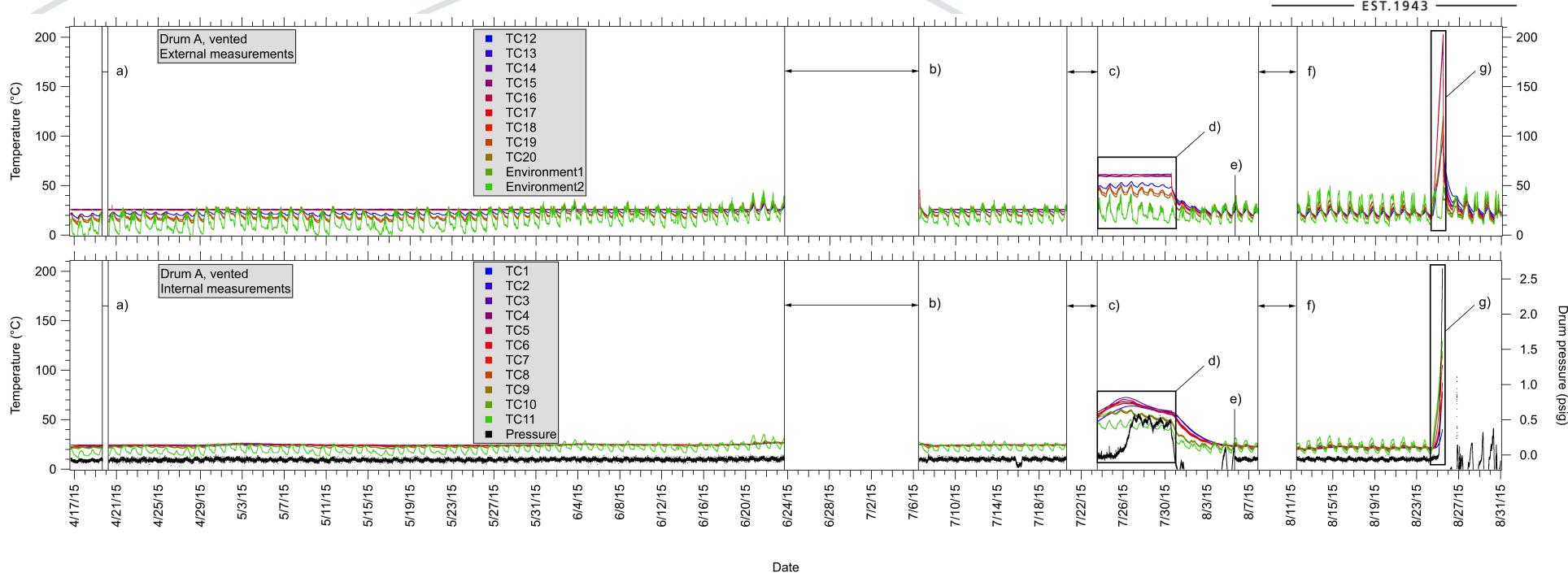


Results

Drum A



Drum A (25°C, vented): Full dataset



This drum represents the normal storage conditions for an RNS drum in the WIPP

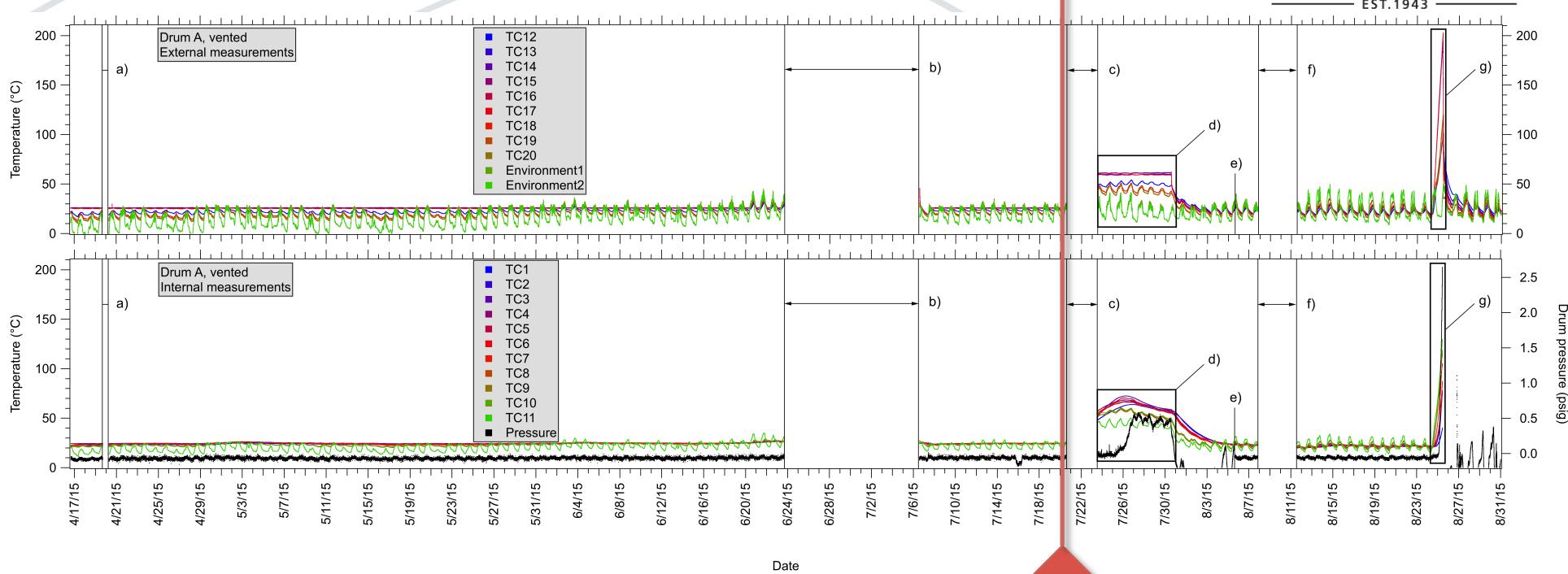


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Drum A (25°C, vented): Full dataset



After ~94 days without signs of self-heating, facility was lost and controller reset to 60°C.

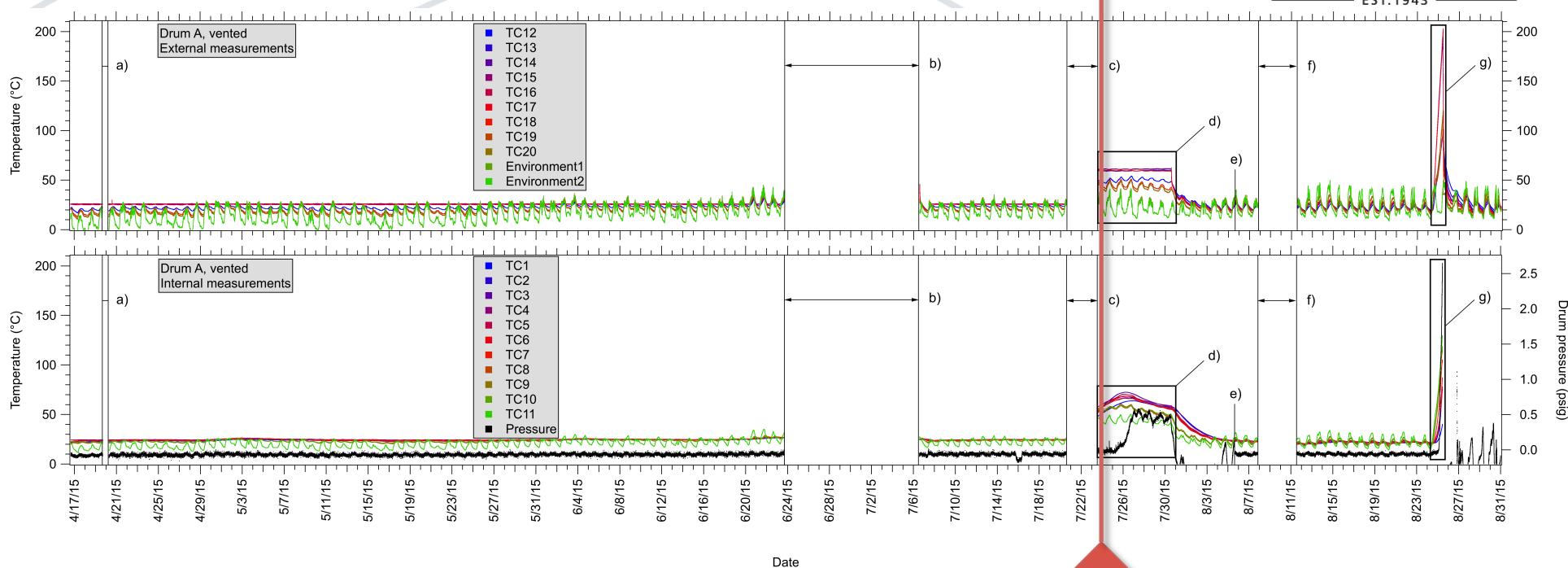


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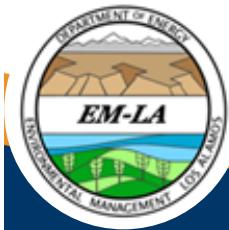


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Drum A (25°C, vented): Full dataset



After 3 days at 60°C, the contents began to self-heat, but quenched.

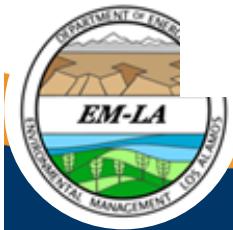
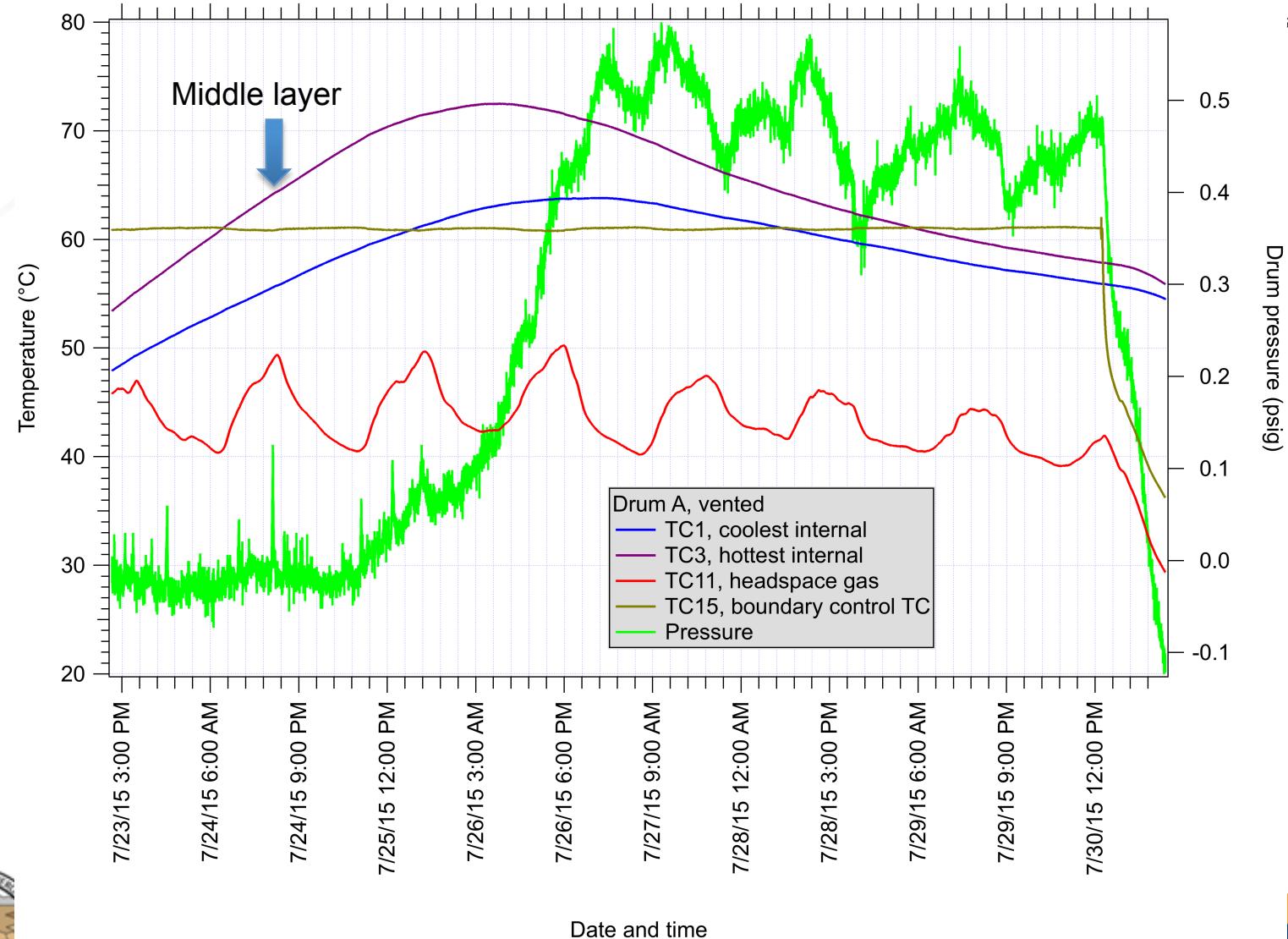


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Drum A (25°C, vented) self heating-quench event: detail

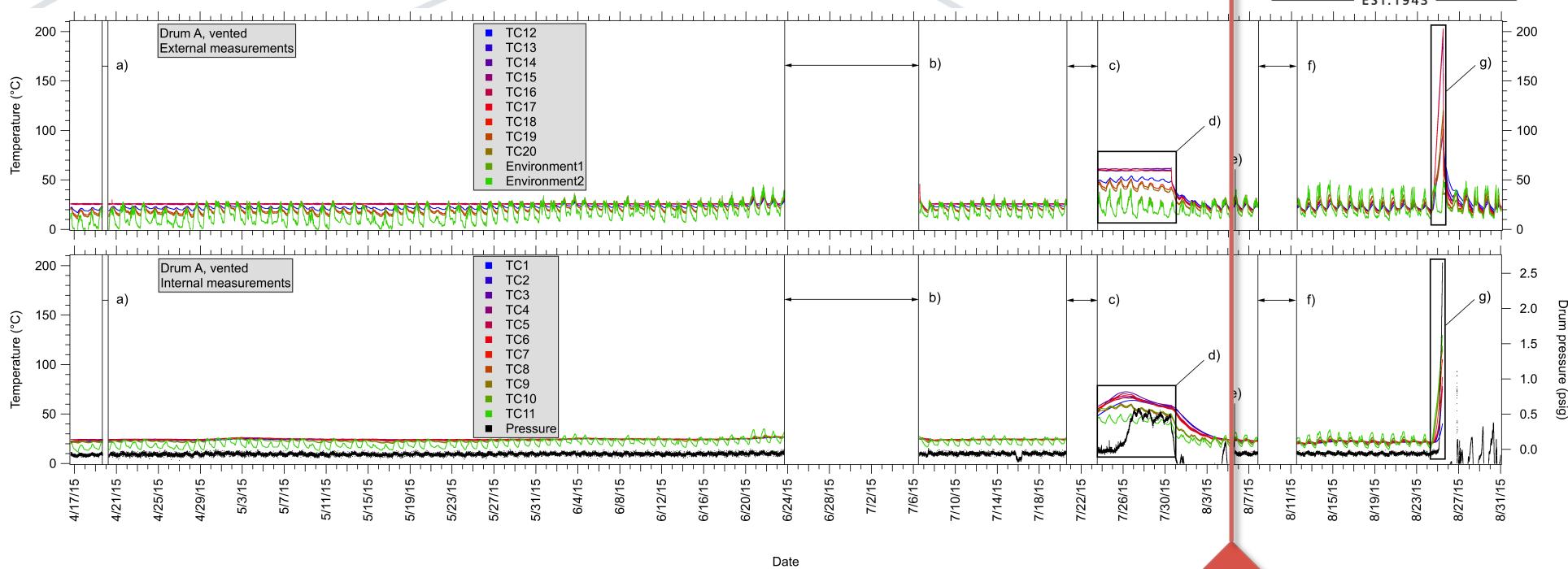


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Drum A (25°C, vented): Full dataset



Heater was turned off and drum was opened for examination of contents.



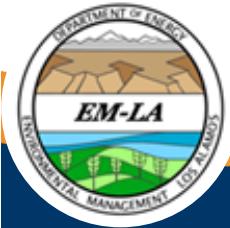
Operated by Los Alamos National Security, LLC for the U.S. Department of Energy's NNSA



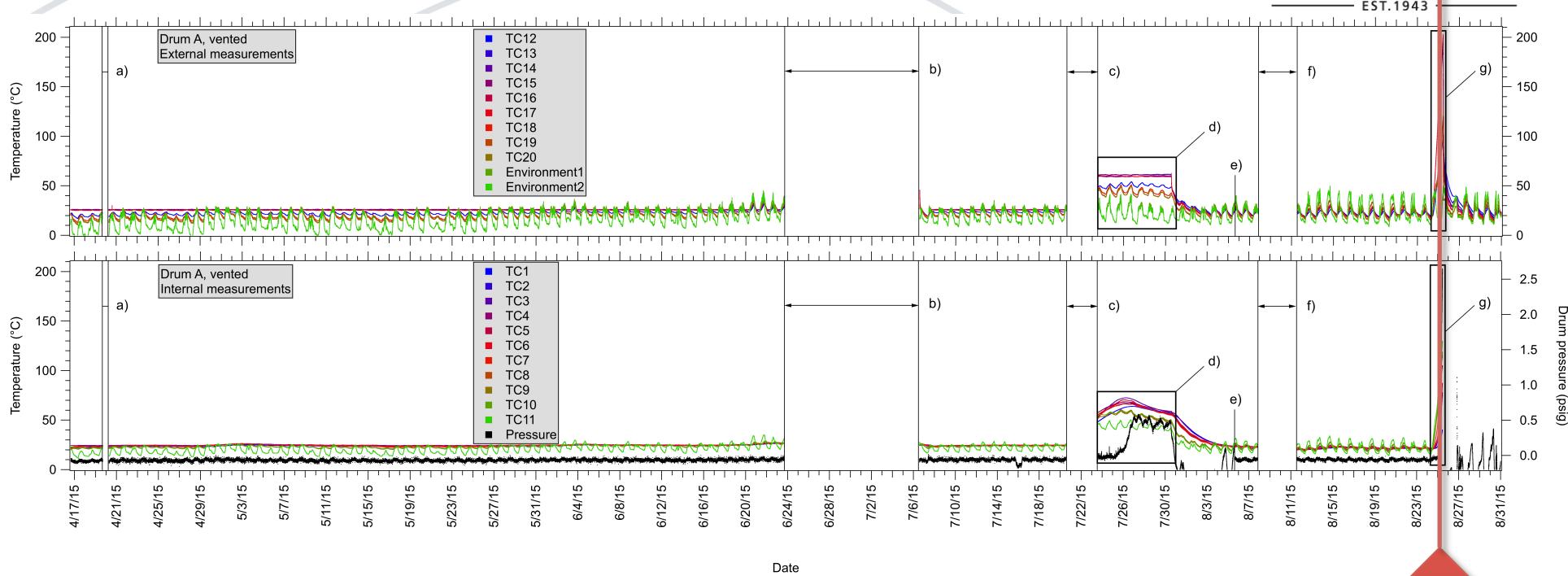
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Drum A (25°C, vented): Post-mortem

- Lid was intact
 - Corrosion present
- Bag slightly yellowed
- Contents were heterogeneous and damp
 - Material had reddened slightly, but otherwise looked like its original condition
- Likely the reactive potential still existed



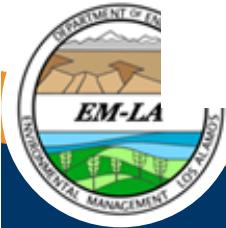
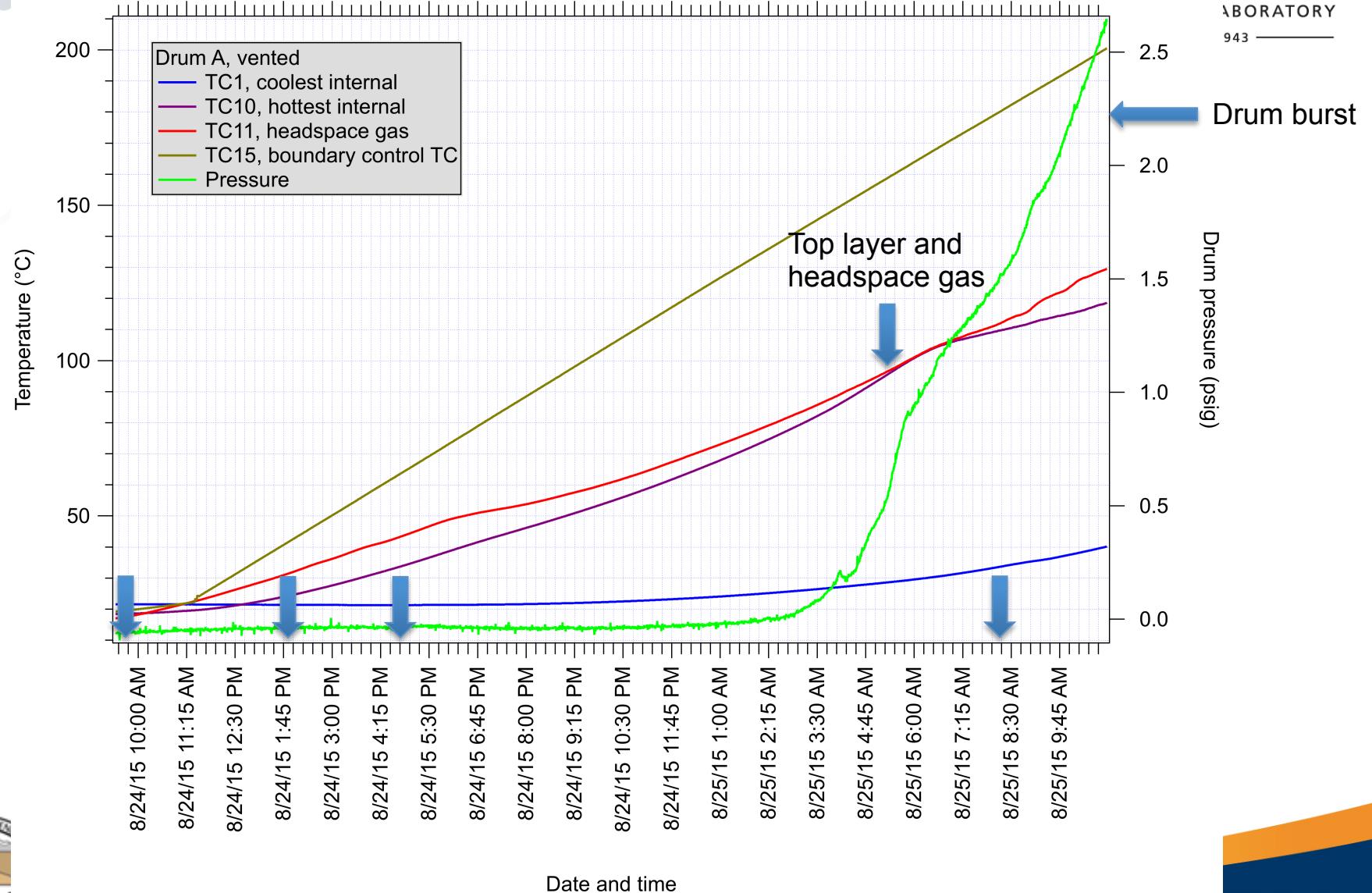
Drum A (25°C, vented): Full dataset



Drum was heated to 200°C to render the contents safe. Reaction was observed.



Drum A (25°C, vented) self heating-quench event: detail



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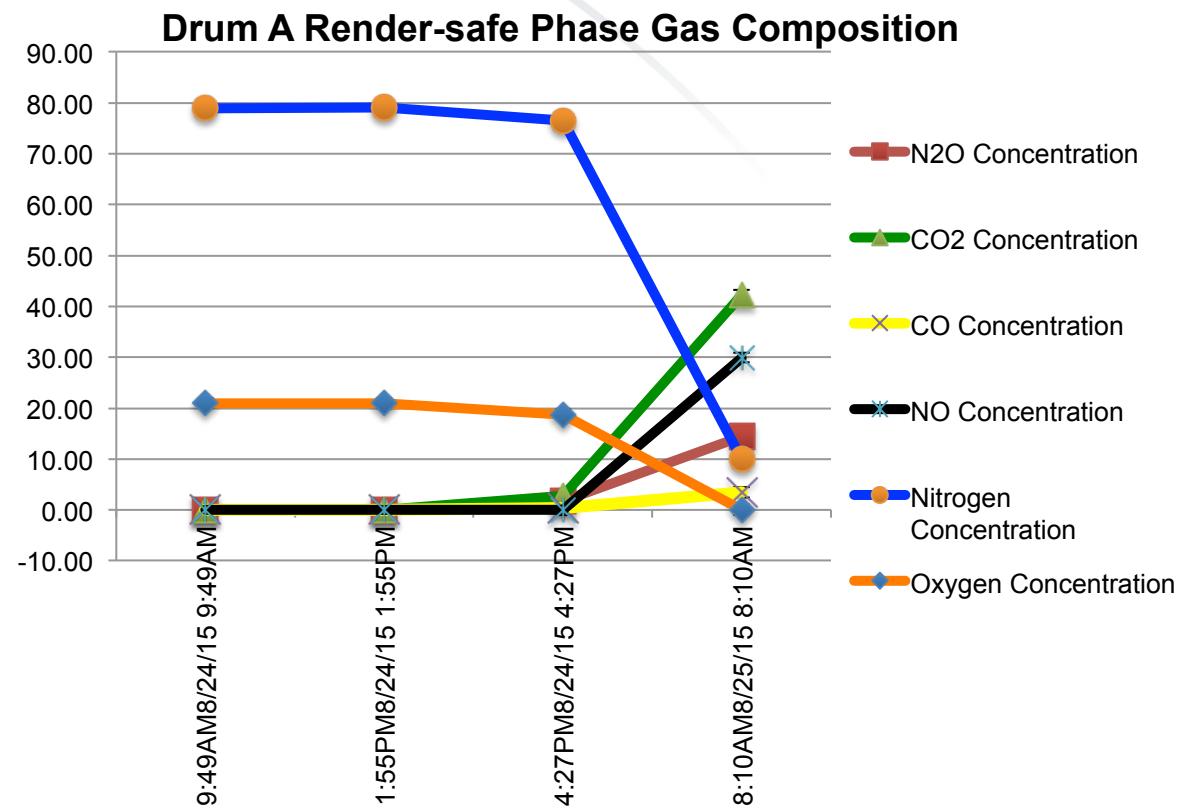


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Drum A (25°C, vented): headspace gas analysis

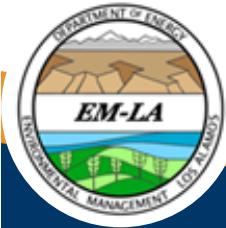


- The nitrogen observed is attributed to nitrogen from ambient air. Other gases observed were likely displacing the nitrogen as they were generated within the drum.
- Significant quantities of NO, N₂O and CO₂ were measured.
- Oxygen was gradually depleted until it was not detected in the sample above the reporting limit of 30 mtorr.
- NO₂ cannot be measured directly with the GC/TCD, though pressure balance might indicate very little concentration.



Drum A: Summary

- In first 94 days, lack of measurable temperature rise shows that a normally configured drum should be able to adequately dissipate heat and products gases so that thermal runaway is not possible.
- After 94 days, upon heating to 60°C, self-heating began showing that reactive potential remained. However, even these reactions quenched.
- Upon heating to 200°C, there was evidence of combustion after internal temperatures exceeded 120°C.
 - Sudden rupture of the drum and dispersal of glowing embers.



Discussion: Comparisons



- Drum A (vented) vs. Drum B (sealed), both at 25°C
 - Drum B showed pressure rise from the start and self-heating after 12 days. Drum A showed neither.
 - Suggests reaction is occurring at 25°C, but slowly.
 - Key points:
 - If vented, the heats of reaction and product gases are dissipated to the environment efficiently and reactive NO_x gas concentrations stay low. Low-temperature NO_x-producing reactions eventually deplete reactants.
 - If sealed, reactant gas concentration increases as do kinetics. This low-temperature chemistry does not, however, liberate enough heat energy to self-heat the mass up to the next “rung” on the notional “ladder” of ever-higher-temperature reactions.
 - These drums were insulated, whereas actual drums are not.



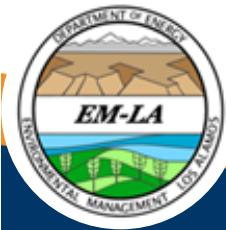
Discussion: Comparisons

- Drum C (vented) vs. Drum D (sealed), both at 60°C
 - Drum D exhibited thermal runaway and pressure burst. Drum C did too, but only so long as gas flow was restricted or blocked. Once pressure was relieved, thermal runaway was halted (at 115°C).
 - Remarkable turnaround late in the runaway.
 - Key points:
 - Two conditions—a blocked vent *and* elevated temperature—were required to cause thermal runaway and drum breach.
 - Neither blockage, nor 60°C boundary temperature, alone caused breach.



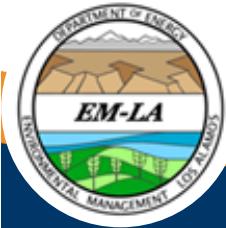
Discussion

- If Drums A & B did *not* undergo thermal-runaway-to-ignition, why did Drum 68660?
 - Surrogate-filled drums had more water
 - A critical fraction of heat energy was partitioned into water's heat capacity and latent heat of vaporization, hence was unavailable to raise the temperature of the bulk sufficiently to access the next rung of the "ladder".
 - Our surrogate mixture had higher activation energy than the contents of Drum 68660
 - Recent formulations (e.g. SFWB11) shows lower temperature activation and higher reaction rates.
 - The drum contents—both physical and chemical makeup
 - are widely variable and Drum 68660 had a rare combination that put it on the tail of the distribution of potential compositions.
 - With this possibility, and the fact that no other drums have behaved similarly, statistical analysis can be attempted.



Conclusions from the full scale tests

- These tests demonstrated thermal runaway and drum rupture with a plausible surrogate nitrate salt/Swheat mixture
 - Supports the hypothesized “ladder” of reactions
 - Evidence supports the hypothesis that NO_x product gases from hydrolysis of metal nitrate salts are responsible for exothermic oxidation of the organic pet litter.
- Pressurization is required for runaway
 - Very sensitive to gas concentration (correlated with pressure).
- Reactant concentrations for the low-temperature chemistry can be diminished with sufficient time at ambient temperature.
 - Likelihood for bootstrapping up to the next higher-temperature chemistry goes down.
 - This does not mean that higher-temperature reactions can't be activated if external heating is applied. In fact, we have shown this can happen.
- Accident prevention strategies include:
 - Elimination of the potential for pressurization.
 - Reduction in storage temperature.

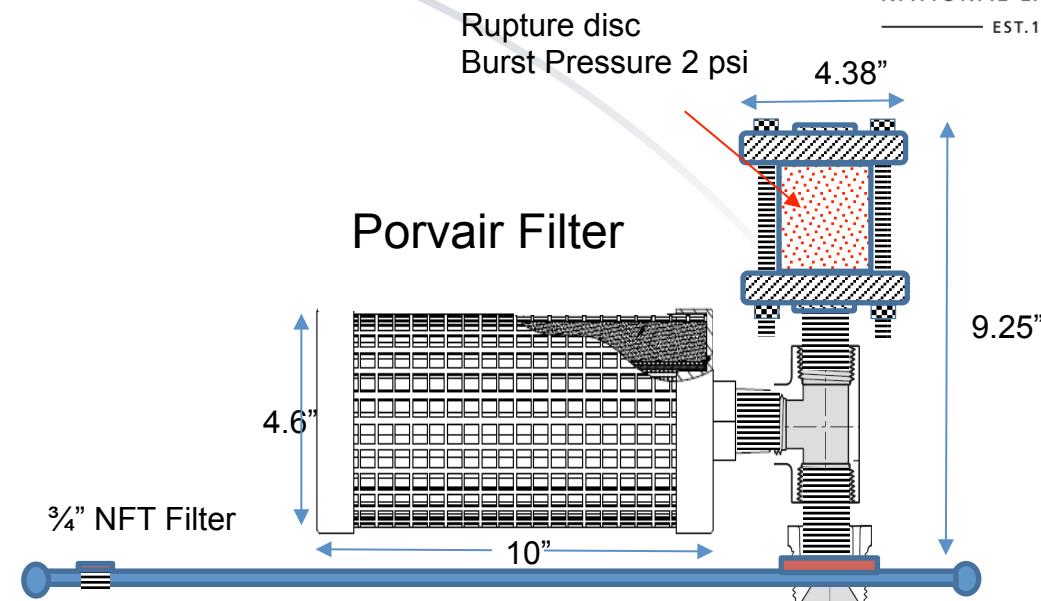


Strategy for enhanced safing is being developed



Estimate Flow of Gas in Large Drum Tests

time	Temp	Pressure	Flow Rate
hrs	°F	psig	l/m cfm
24	73	0.7	0.003 0.000
48	84	2.0	0.012 0.000
60	82	3.7	0.020 0.001
62	89	4.8	0.055 0.002
64	96	5.2	0.063 0.002
66	101	6.5	0.104 0.004
68	104	8.7	0.214 0.008
70	106	13.3	0.430 0.015
72	110	21.7	1.16 0.041
72.6	146	30.9	2.75 0.1



Rupture Disc



Holder



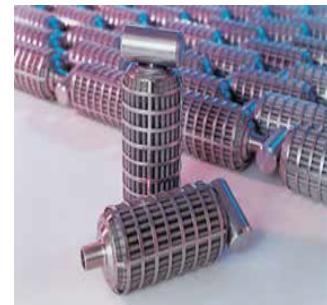
Disc

1.5 to 10 psi



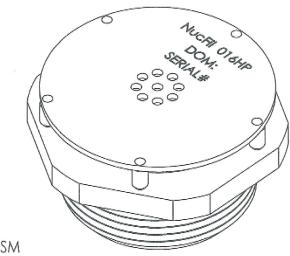
Porvair Filter

91,000 ml/m @ 1 " WC
3.25 CFM @ 1" WC



NFT Filters

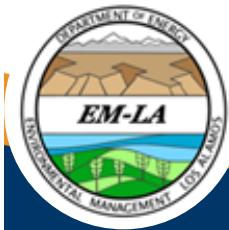
3/4" NFT = 200ml/m @ 1 " WC



NPSM

Small Scale Follow-On Work

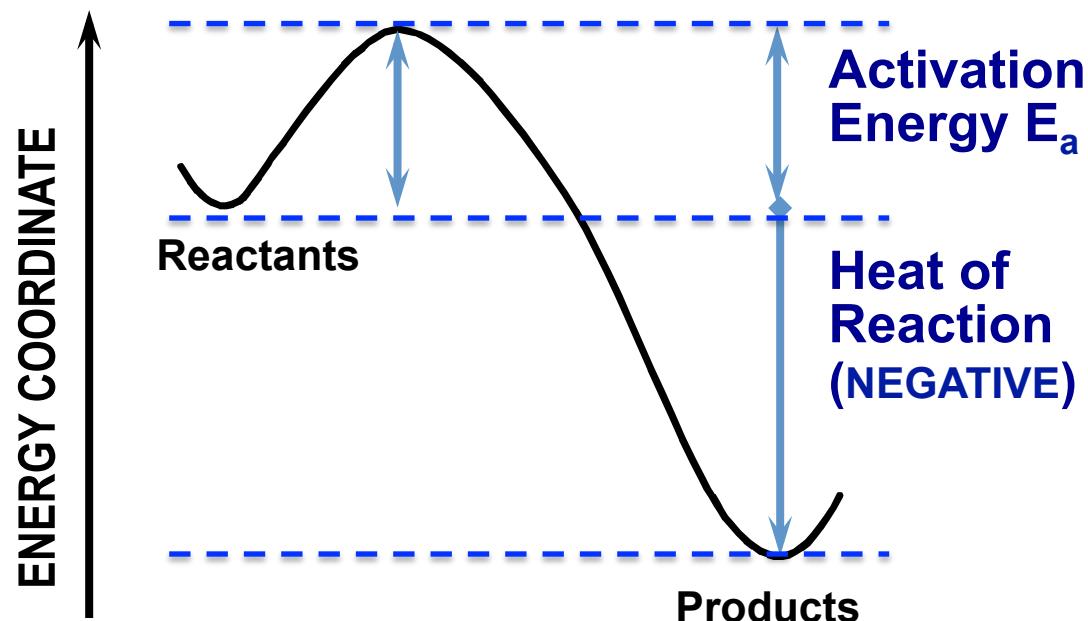
- Validate thermal sensitivity decreases with time
 - Simply put, the lower the onset temperature, the more reactive the the species and the greater their subsequent depletion at ambient temperatures
- Investigate whether agitation can reset drum contents (and to what level); significant concern about this
 - Plan:
 - Prepare 12 or more salt/swheat mixtures in Nalgene bottles equipped with NFT filters
 - Once a week test with APTAC to evaluate whether we observe increasing/decreasing thermal/ignitability behavior
 - At the end of the test period (12 weeks), we can shake them and retest a subset, to observe the effect of agitation



Temperature Control Strategy: Technical Basis

Arrhenius equation – first order kinetics:

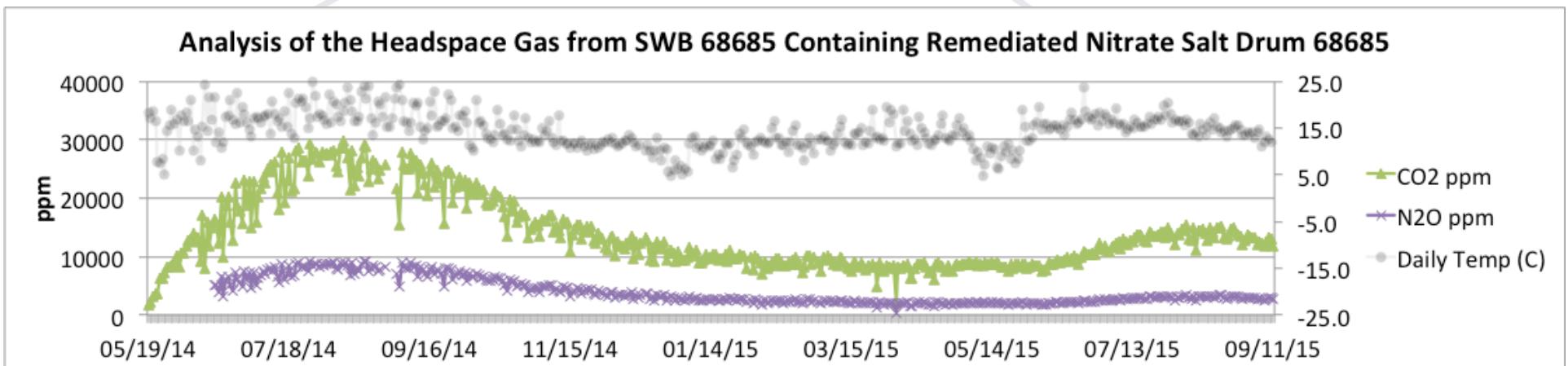
$$k(T) = A e^{(-E_a/RT)}$$



Energy diagram for exothermic reaction



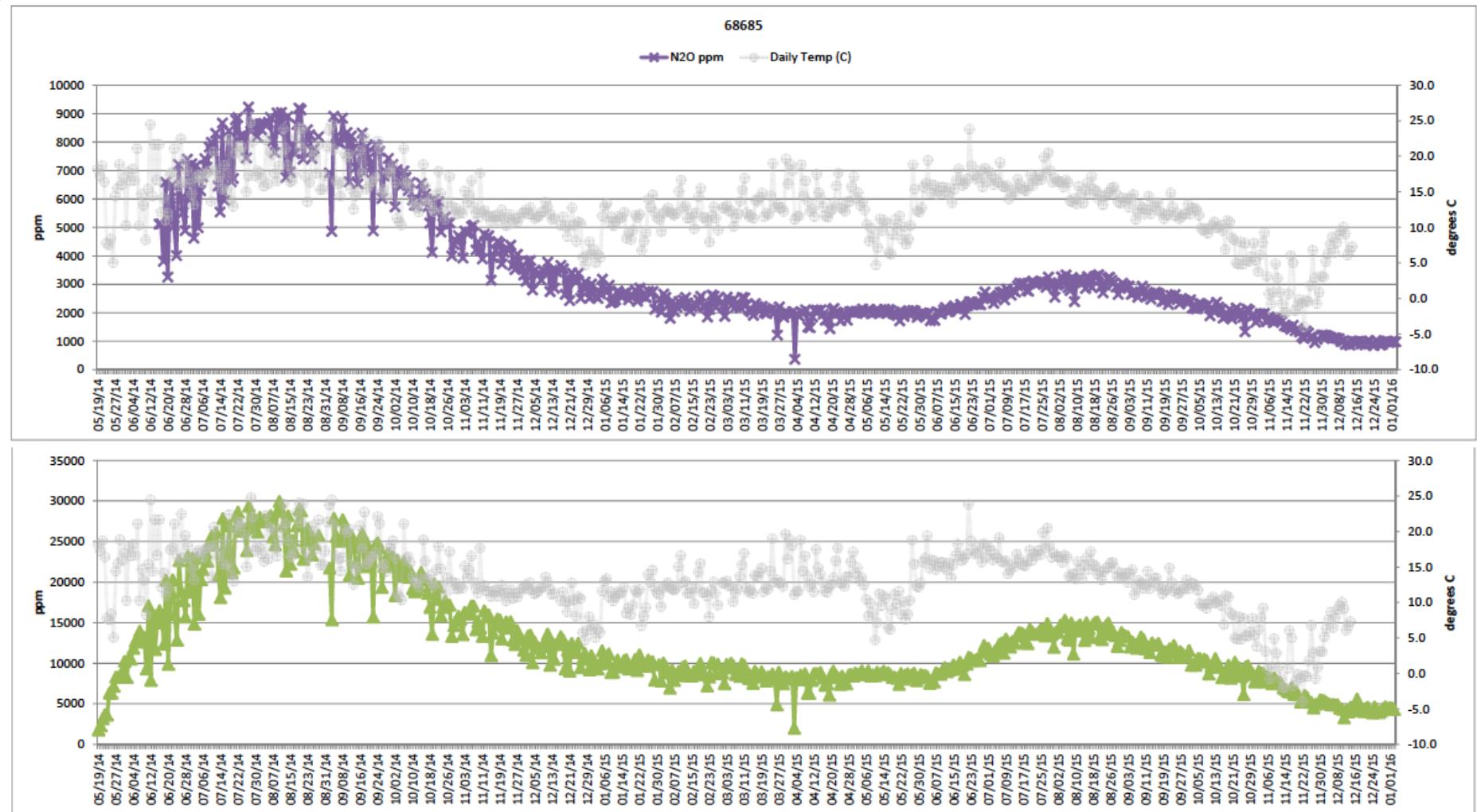
Temperature Control: Headspace Gas Analysis Indicates Decreasing Reactivity



- Robinson developed a model of headspace gas concentration that includes chemical reaction production, venting, and air exchange
- The model yielded activation energies of ~15-20 kcal/mol and heat generation rates of less than one Watt (Summer of 2014)
- Qualitatively, thermal runaway requires increasing chemical reaction and heat production – decreasing concentrations would suggest that we are on the “back side” of the reactivity curve



Temperatures and the correlated N₂O and CO₂ concentrations are at their lowest points ever



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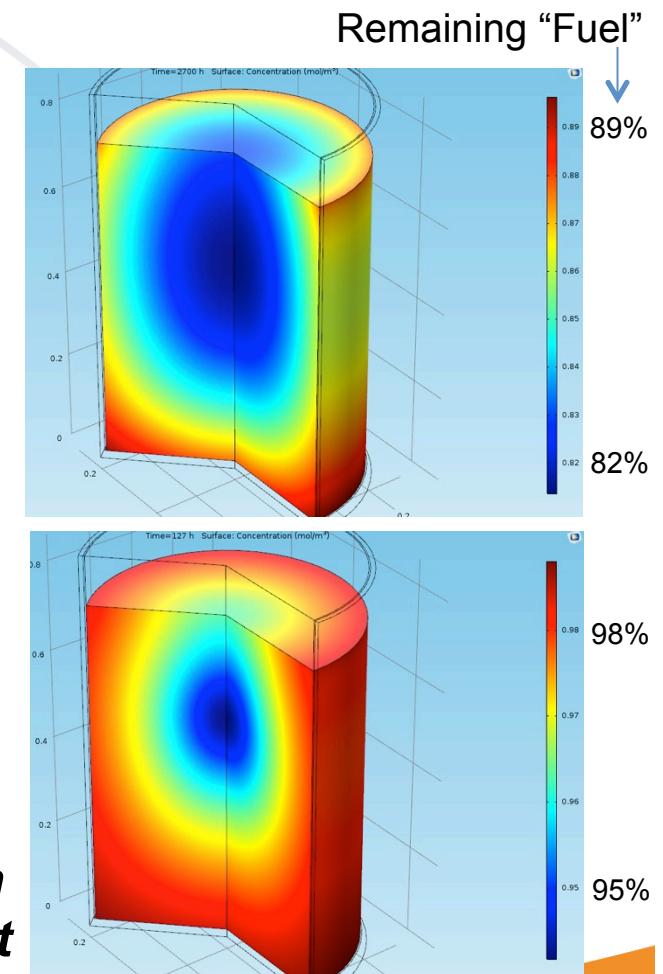
Temperature Control: simulation of drum kinetics

25 °C: no runaway after 2700 hours (top)

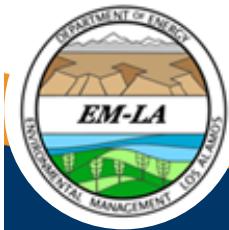
30 °C: runaway after 127 hours (bottom)



- Drum modeled as containing homogenous contents obeying single Arrhenius kinetic rate:
 $k=A \cdot e^{-E_a/RT}$
 - Thermal conductivity derived from cold temperature tests (precise measurements in process)
 - Legend is fraction of reactants remaining
- Identical kinetics used in both calculations on right: 5 °C makes the difference between “go” and “no-go”
- Sensitivity has explored by varying A and E_a identifying those parameters that support runaway (“go”)
 - Nonphysical parameters ruled out



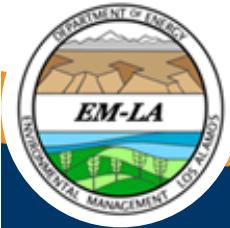
Analysis supports our current hypothesis of drum behavior (safety increases with time, barring upset conditions): defense-in-depth



Temperature Control: Finalize process parameters using modeling informed by experiment



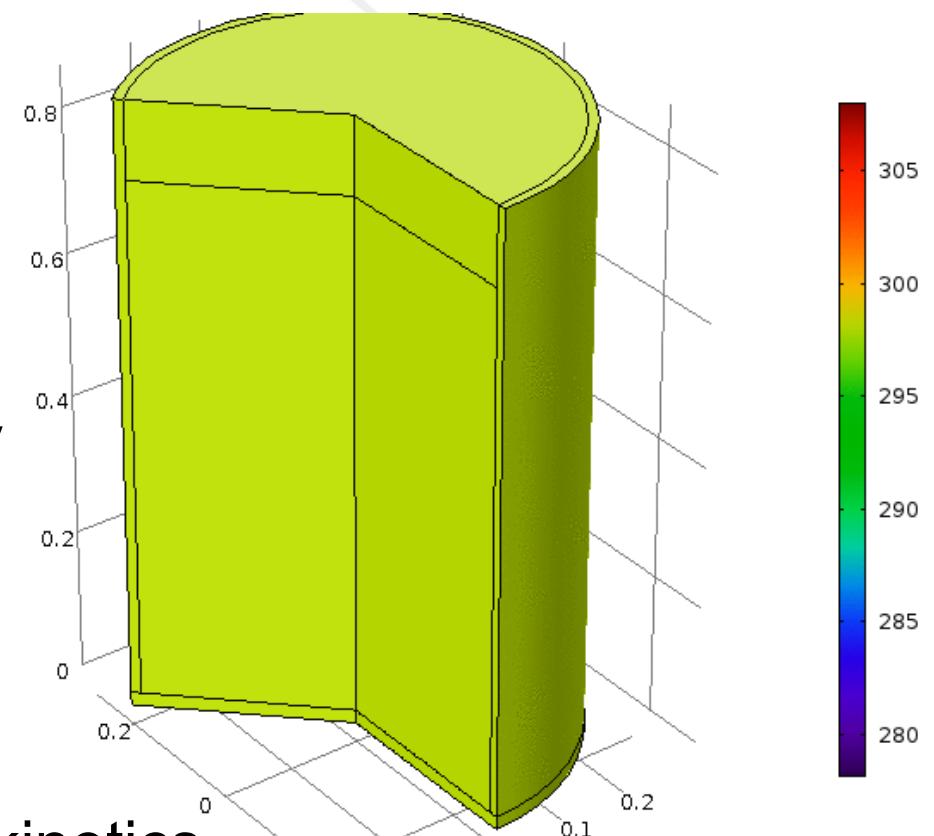
- Automatic Pressure Tracking Adiabatic Calorimetry (APTAC) will be used to determine thermally sensitive surrogate and establish kinetic parameters (NQA-1 Test Plan:PLAN-TA9-2243)
 - APTAC testing being conducted
 - Feeds COMSOL modeling effort
 - Finalize process parameter selection
- Differential Scanning Calorimetry (DSC) will be used to compare surrogates spiked with actinides and those created using UNS samples
 - Data expected to validate use of surrogates and evaluate effect of actinides on thermal sensitivity (use TA-55 procedures; PMT2MPRDOP-015)



Temperature Control: Simulation is guiding our process parameter selection



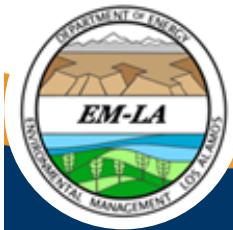
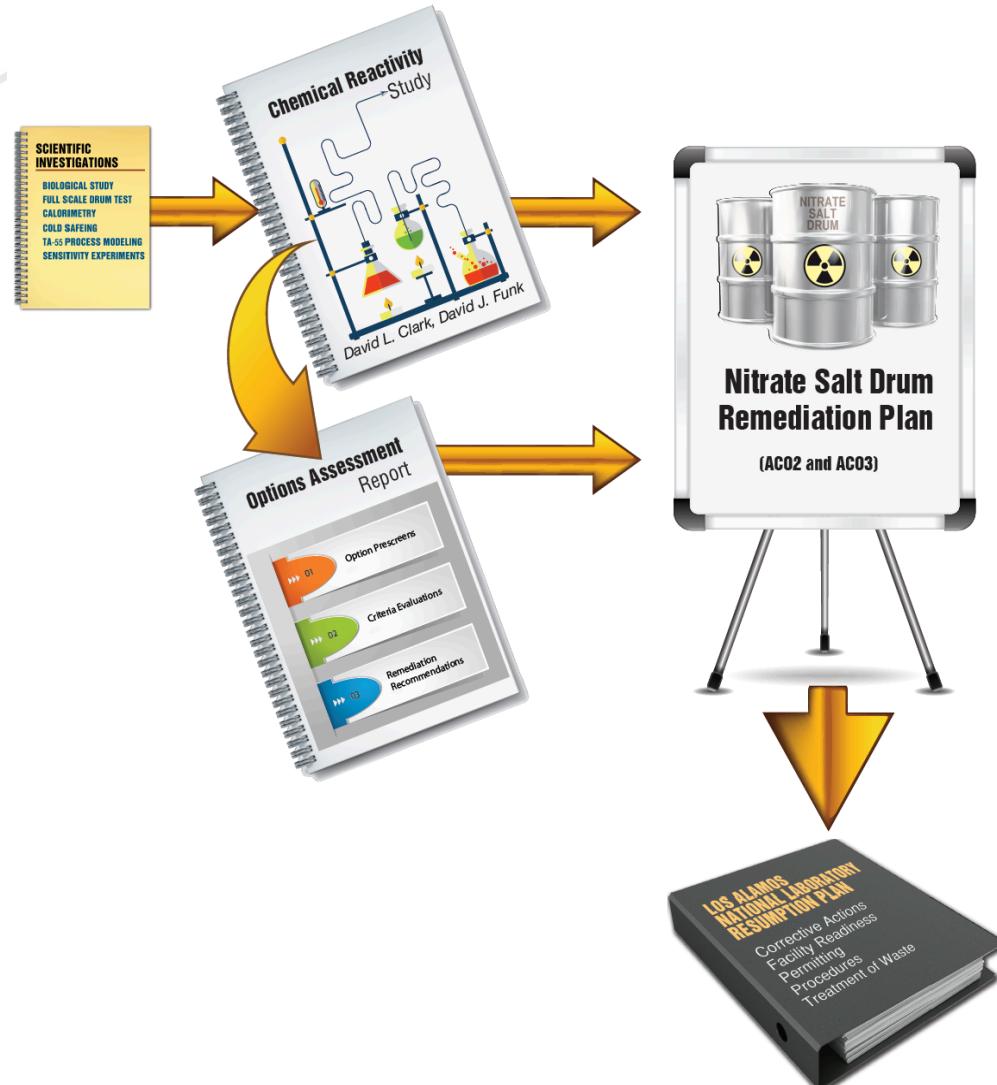
- Drum with homogenous contents exhibits thermal runaway in 12 days @ 25°C
- On day 11 of the simulation, the drum is placed in a refrigerator at 5 °C (boundary condition changed)
- The drum does not exhibit runaway



APTAC data generates kinetics,
COMSOL used for simulation



A Panel of Experts Assessed Treatment Options for the Nitrate Salt Waste

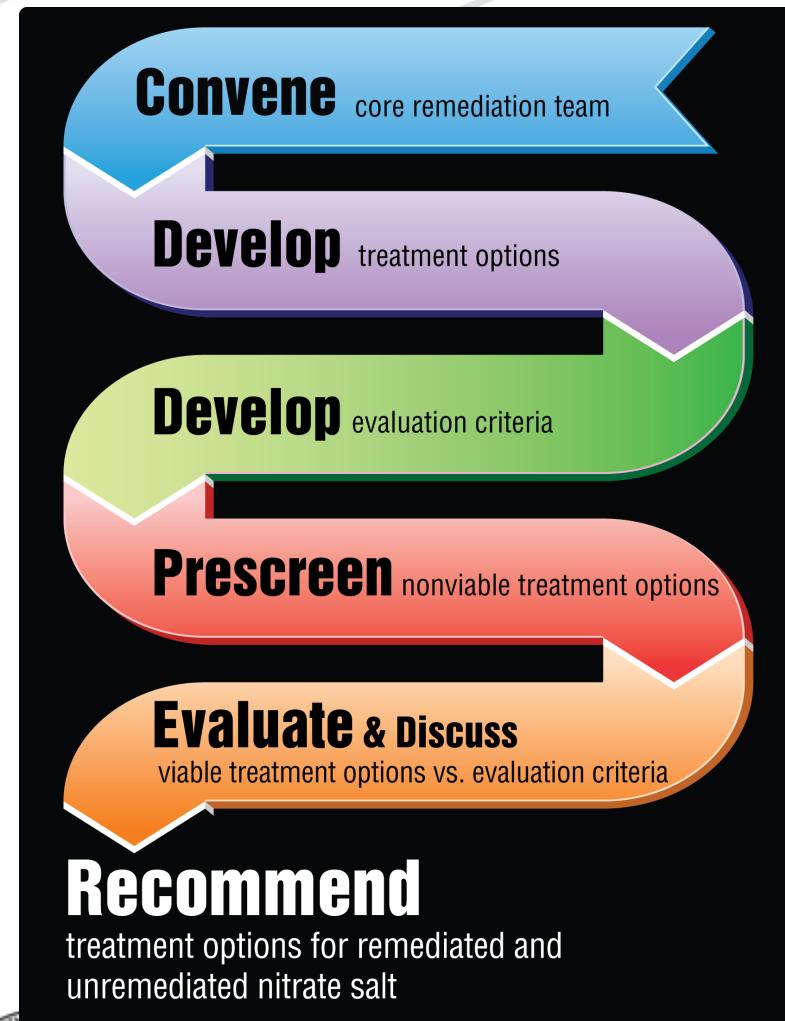


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Core Team Process



Bruce Robinson Lead

David Clark Technical Advisor
David Funk Technical Advisor

Enrique Torres	Benchmarking
Philip Leonard	Energetic Chemistry
Stephen Yarbro	Actinide Chemistry
Robert Wingo	Cementation
Scotty Miller	Operations
Steve Clemons	Operations
Gian Bacigalupa	Regulatory
John Hopkins	Regulatory
Faris Badwan	Quality Assurance
Randall Erickson	ADEP
Kapil Goya	TA-55 Waste Expert
Jeff Carmichael	TA-55 Waste Expert
Andrew Baumer	FOD
Charles Conway	FOD
Rick Alexander	FOD
Robert Stokes	ES&H
Ronald Selvage	Safety Basis
Timothy Burns	Carlsbad RSO
Christopher Chancellor	Carlsbad RSO
Patrice Stevens	Project Management

Independent peer review was important for completeness

Treatment Options were scored



EVALUATION CRITERIA

POTENTIAL TREATMENT OPTIONS	Evaluation Criteria												Score
	Robust to waste stream variability	Ease of permitting (permitting difficulties)	Safety basis challenges	Extent of testing required	Reduction of toxicity and mobility	Reduction in volume	Short-term and long-term effectiveness	WCS implications	Scalability and complexity	Facilities challenges	Schedule	Cost (not a primary evaluation criterion) *	
1 Stabilization Using Zeolite (remediated)	5	3	4	5	4	2	4	2	4	4	4	4	41
1 Stabilization Using Zeolite (unremediated)	5	3	4	5	4	2	5	N/A	5	5	5	5	43
2 Stabilization Using Zeolite With Cementation (remediated)	5	2	3	3	4	1	4	1	2	2	1	1	28
2 Stabilization Using Zeolite With Cementation (unremediated)	5	2	3	3	4	1	5	N/A	3	3	2	1	31
3 Stabilization Using Dry-Process Cementation (remediated)	5	2	2	3	4	3	4	1	3	2	2	2	31
3 Stabilization Using Dry-Process Cementation (unremediated)	5	3	2	3	4	3	5	N/A	4	3	3	3	35
4 Stabilization Using Wet-Process Cementation (remediated)	3	4	1	3	4	2	4	1	1	1	1	2	25
14 Salt Dissolution With Cementation/Stabilization (remediated)	3	3	1	3	4	2	4	1	2	1	2	2	26
5 Incineration													
6 Thermal Oxidation of Organics													
7 Biodegradation													
8 Chemical or Electrolytic Oxidation													
9 Chemical Reduction													
10 Vitrification													
11 Alternate Macro-Encapsulation													
12 Neutralization													
13 Controlled Reaction or Leaching of Reactive Inorganic Chemicals With Water													



Zeolite addition or cementation are the top treatment recommendations for both unremediated and remediated nitrate salts



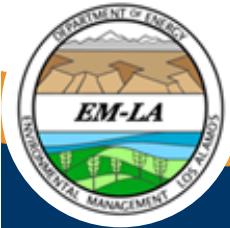
RCRA Stabilization Options	
1. Stabilization Using Zeolite	Mix waste into inorganic natural mineral to eliminate ignitability potential of the waste
2. Stabilization Using Zeolite With Cementation	Option 1 followed by production of cement waste form
3. Stabilization Using Dry-Process Cementation	Production of cement waste form with water added only at the time of cementation
4. Stabilization Using Wet-Process Cementation	Initial water addition to eliminate potential thermal runaway reactions, followed by production of cement waste form
14. Salt Dissolution With Cementation/ Stabilization	Water addition followed by filtration and cementation process of Swheat™ cake and nitrate salt solution
Other RCRA Options	
5. Incineration	Burning of waste in a radiological incinerator
6. Thermal Oxidation of Organics	Treatment of waste in air to oxidize without flame
7. Biodegradation	Biological breakdown of organics or non-metallic inorganics under aerobic or anaerobic conditions
8. Chemical or Electrolytic Oxidation	Breakdown of organics through the addition of oxidation reagents
9. Chemical Reduction	Breakdown of nitrate constituents through the addition of reducing reagents
10. Vitrification	Incorporation of waste into a glass waste form
11. Alternate Macro-Encapsulation	Coating of the waste with an organic polymer to reduce surface exposure
12. Neutralization	Reagent addition to neutralize the pH
13. Controlled Reaction or Leaching	Removal of soluble salts by leaching with water



Treatment methodologies are being evaluated for efficacy to support permit mod request

- EPA testing methodologies are being used to evaluate RCRA Characteristics of Ignitability (D001) and Corrosivity (D002)
 - Southwest Research Institute (SwRI, EPA Certified Lab)
 - Conduct SW-846 1030 (burn rate), 1050 (spontaneous combustion), UN DOT O.1 and O.2 (oxidizers), 9095B (liquids) tests
 - Initial testing in progress
 - Tests include controls and treated surrogates
 - Nitrate salts mixed in various ratios with Swheat and then mixed with zeolite (1:3) or grout
 - Initial results are confirming that the remedy is effective

After demonstration, need engineered implementation

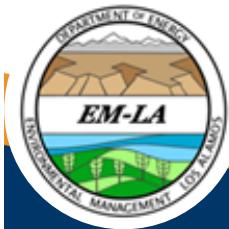


An Engineering Options Assessment was Conducted



- Evaluation Approach
 - Characterize Waste Streams
 - RNS, UNS
 - Examine Treatment Approaches
 - Blending & Cementation
 - Evaluate Remediation/Repackaging Systems
 - WCRRF, Modulars, Gloveboxes at TA-54
 - RNS and UNS streams
 - Remaining Legacy Waste

We will be taking an additional look at our options using a broad, national team of experts



Preferred Process Options



1. **Drum blending** is easiest, fastest, best ALARA option
 - Concerns related to quality of blend and verification of mix quality
2. **Batch blending** is simple, slower than drum blending
 - Zeolite introduce in daughter drum
 - Operators will get more dose compared to drum blending
3. **Cementing in a drum tumbler**
 - Eliminates adding cement in the glovebox
 - Still requires dissolution and pH adjustment in drum
4. **Cementing in glovebox** is most difficult option
 - Add cement in glovebox
 - Mix cement in glovebox
 - Sacrificial agitator



Preferred Process Options



1. **Batch blending** is simple, slower than drum blending

- Zeolite introduce in daughter drum
- Operators will get more dose compared to drum blending
- Only a 60 Drum Campaign for RNS

2. **Drum blending** is easiest, fastest, best ALARA option

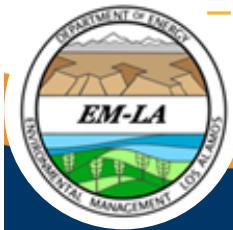
- Concerns related to quality of blend and verification of mix quality
- Time to prove-in likely extensive

3. **Cementing in a drum tumbler**

- Eliminates adding cement in the glovebox
- Still requires dissolution and pH adjustment in drum

4. **Cementing in glovebox** is most difficult option

- Add cement in glovebox
- Mix cement in glovebox
- Sacrificial agitator



Blending process has been developed



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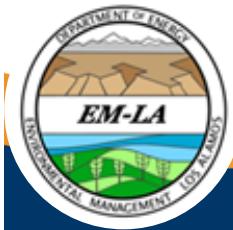


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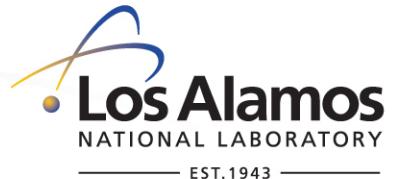
Remediation/Repackaging Systems



- Waste Characterization, Reduction, and Repackaging Facility
 - Restart WCRRF and use glovebox
- Modulars
 - MOBILE Visual Evaluation and Repack (MOVER)
 - MOBILE Repack (MORK)
- Add Glovebox at Area G
 - 2 candidates in storage @ TA-54
 - MORK type glovebox
 - Relocate WCRRF glovebox



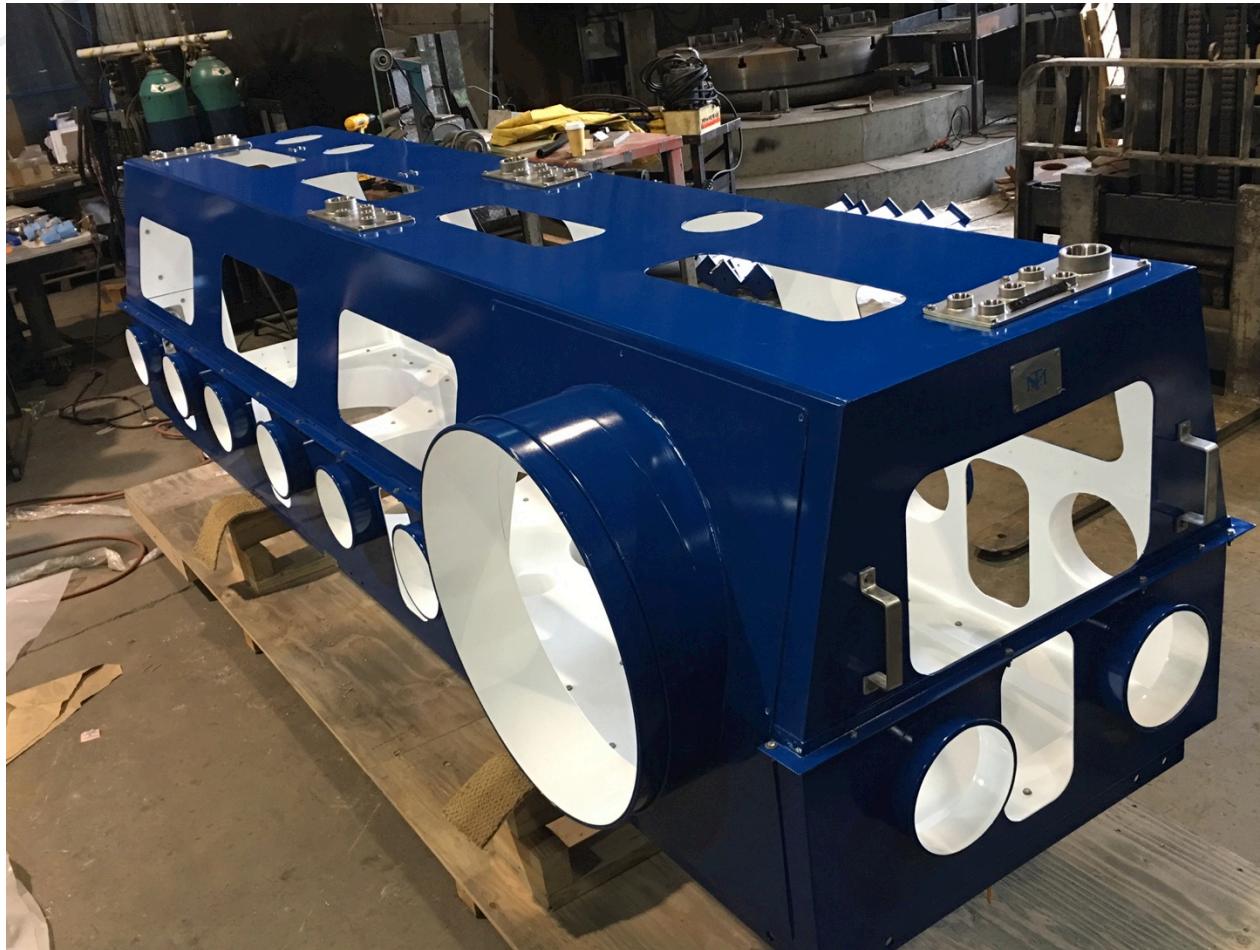
System Evaluation



	Blending	Cementation	Debris Waste	RNS & UNS	Drums	Legacy Drums	AB Issues	RCRA Issues	Installation	Fabrication	Readiness	Operation	Schedule	Cost	Total
WCRRF	3	3	4	5	5	4	3	4	5	1	3	4	4	48	
MOVER	3	1	2	5	4	4	3	4	4	1	3	3	3	40	
MORK	3	2	5	5	5	2	1	2	3	1	4	1	2	36	
GB 1121	5	5	5	3	3	3	3	3	2	1	4	3	3	43	
GB 412	4	4	2	3	3	3	3	3	4	1	4	4	4	42	
MORK GB	4	4	4	3	3	4	3	3	1	1	5	2	1	38	
WCRRF GB	3	3	4	3	3	4	3	2	3	1	4	4	2	39	



We have developed a mock box a for process prove in and to develop proficiency



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System Options – Nitrate Salts



1. WCRRF Glovebox – Class 2 Permit Mod

- Long track record
- Infrastructure in place and tested
- Glovebox in place and tested
- BIO in place needs adjustment to handle oxidizers
- MAR limit is 800 ECPE –Ci
- Haz Cat 2 Facility – Safety Significant glovebox (Safety Class?)

2. Glovebox in Area G – Class 3 Permit Mod

- Pedigree of glovebox
- 18 ECPE-CI limitation
- Modifications and configuration issues
- Safety basis challenges

***Need Safety Basis Strategy to support
engineered implementation***



Summary of the Anticipated Control Set for RNS Processing

- Temperature and Pressure Control: Mitigate the Possibility of Thermal Runaway During Handling
 - Work conducted to support temperature and pressure controls
 - Head Space Gas Analysis
 - Modeling – COMSOL Simulations and Small Scale APTAC studies
 - Full Scale Drum Testing – Small Scale Follow-on
- Credited Glove Box: Protection During Treatment of Waste
 - Evaluate WCRRF to validate adequacy under credible accident scenarios – can contents runaway in DBAs?
- Processing Order of the Drums
 - Process in order of increasing consequence
 - Quantity of Salt/Swheat influences consequence and likelihood



Control: Processing Order of Drums

- Thermal runaway also depends on the quantity of material and configuration (geometry)
- We can minimize consequence and establish additional confidence in our understanding by processing drums with low volume/mass of salt/Swheat mixture (and likely low MAR) and low probability of runaway

Values		
Row Labels	Count of Container	Sum of Total All Inorganic (kg)
LA-CIN01.001-Cans	1	143.1
75-100%	1	143.1
LA-MHD01.001	12	426.2
0-25%	5	57.1
25-50%	6	355
50-75%	1	14.1
LA-MIN02-V.001	47	4418.2
50-75%	5	282.3
75-100%	42	4135.9
Grand Total	60	4987.5

Row Labels	Count of Container
LA-CIN01.001-Cans	1
SWB-55	1
LA-MHD01.001	12
POC	2
SWB-55	10
LA-MIN02-V.001	47
POC	2
SWB-55	37
SWB-POC	8
Grand Total	60



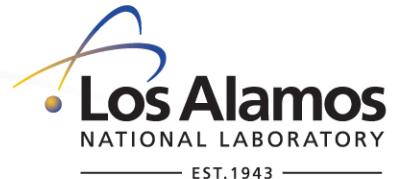
Summary of the Overall Steps for Treatment of Nitrate Salt Wastes



- Temperature and Pressure Control – Safing
 - Implement supplemental cooling to keep waste cool
 - Open SWBs, add vent/pressure relief to prevent accident – our top priority
- Treatment of Waste – Stabilization (zeolite/cement)
 - Treatment Study
 - Complete testing of treatment option and final waste form using surrogates
 - Spike surrogates with actinides, sample unremediated nitrate salt waste and combine with Swheat
 - Conduct comparison studies of thermal sensitivities
 - Develop Engineered Implementation
 - Treat the nitrate salt wastes: stabilization using zeolite addition or cementation



A Senior Integrated Project Team (IPT) has been stood up:



- Dave Nickless (EM-LA) and Dave Funk (LANL) co-leads
- Contracting: Chris Lockhart (EM-LA) and Jerry Ethridge (LANL)
- Safety Basis: Jim O'Neil (NA-LA) and Derek Gordon (LANL)
 - Mark Kobi, Sharon Walker (LANL)
- Regulatory: Brian Hennessey (EM-LA) and John McCann (LANL)
 - Mark Haagenstad, Luciana Vigil-Holtermann, Susan McMichael (LANL)
- Operational Readiness: Greg Jones (NA-LA) and Mandy Krenek (LANL)
 - Chris Jones (LANL)
- Engineering: Dave Nickless (EM-LA) and Larry Goen (LANL)
 - Julie Minton-Hughes and Kurt Anast (LANL)
- Maintenance: TBD
- Operations: Bill Mairson (LANL)
 - EWMO: Chuck Conway and WD-DL (LANL)
 - Start-up: David Solms (LANL) and David Frederici (LANL)
 - Emergency Preparedness: Bill Gentile (NA-LA) and Marla Brooks (LANL)



Questions?



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